2009

The feasibility of using select landscape species for phytoremediation of cumene and 4-cumylphenol contaminated groundwater

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THE FEASIBILITY OF USING SELECT LANDSCAPE SPECIES FOR PHYTOREMEDIATION OF CUMENE AND 4-CUMYLPHENOL CONTAMINATED GROUNDWATER

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The School of Plant, Environmental and Soil Sciences

by
Kathryn Fontenot
B.S., Louisiana State University 2003
M.S., Louisiana State University 2005
May 2009

ACKNOWLEDGEMENTS

I would like to thank my major professor, Dr. Edward Bush, along with my committee members, Dr. Ralph Portier, Dr. Maud Walsh, And Dr. Paul Wilson who provided extensive support and knowledge. Georgia-Pacific Corporation graciously provided the funding for this project. Also, thanks are given to Dr. Joel Burken, Dr. Don LaBonte, Dr. Jeff Kuehny, and Dr. James Boudreaux who loaned supplies for this research. Special thanks given to Dr. Charles Johnson for his assistance with the germination experiment. Mr. Dexter Fontenot, Ms. Ann Gray, Mr. Byron Braud and Mr. Eric Holland enthusiastically participated in the construction of the greenhouse, collected tissue samples and watered the trees. Thanks to Mr. Mark Wilson for his support in disassembling the greenhouse and help with the full scale planting. Many thanks are given to Ms. Amy Blanchard for providing support with technical formatting of the dissertation. Deep appreciation is given to Ms. Buffy Ashton, Mr. Scott Miles, Dr. Edward Overton and Dr. Robert Wong for training me in water and soil sampling and kindly allowing me use of their laboratory. Many thanks are given to Mr. Swain Munson for his dedication in making this project successful. Thanks for everyday help at the plant to all the Georgia Gulf employees, especially those in the utilities office. Lastly, I thank my family, parents, Kenneth and Marlys Karsh, brother Stephen Karsh, and husband Dexter Fontenot for their abiding love and support of my educational endeavors.

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LIST OF ACRONYMS

B- Boron
BW- black willow
Ca- calcium
cm- centimeter
COC- constituent of concern
Cu- copper
CW- cottonwood
CY- bald cypress
DCM- dichloromethane
EC- electrical conductivity
ERC- eastern red cedar
Fe- iron
gal.- gallon(s)
GC/MS- gas chromatograph mass spectrometer
IRTC- Interstate Technology and Regulatory Council, a group that developed guidance document for phytoremediation applications.
K- potassium
LDEQ- Louisiana Department of Environmental Quality
mg- milligram
Mg- magnesium
mg/kg- milligrams per kilogram or ppm
mg/L- milligrams per liter or ppm
mL- milliliter
mm- millimeter
Mn- manganese
MNA- monitored natural attenuation
mS- milli siemens
Na- sodium
NaCl- sodium chloride
ng/mL- nanograms per milliliter or parts per million
NS2- a Stratum III groundwater monitoring well used to make the water treatments
NS6- a Stratum III groundwater monitoring well used to make the water treatments
NS8- a Stratum III groundwater monitoring well used to make the water treatments
oz- ounce
P- Phosphorous
ppm- parts per million
PSI- Professional Service Industries
S- Sulfur
SMWU- small management waste unit
SP- spruce pine
WO- water oak
Zn- zinc

ABSTRACT

Chemical manufactures are often associated with a negative publicity due to chemical spills that can cause human health problems and environmental pollution. Innovative methods such as phytoremediation in lieu of traditional remediation methods are being researched to determine environmentally friendly options for remediation. Phytoremediation was studied as an alternative remediation method for removal of chemicals in a contaminated groundwater plume in Louisiana. The main constituents of concern in the plume were cumene and 4-cumylphenol. Two pilot phytotoxicity studies were funded to determine an optimum tree species for removal and control of the constituents of concern. A greenhouse and hydroponic system were constructed to test *Taxodium distichum*, *Salix nigra*, *Juniperus virginiana*, *Pinus glabra*, *Populus deltoids*, and *Quercus nigra* for their phytoremediation capabilities. Both phytotoxicity pilot studies covered a nine month growing period. Trees in the first study were subjected to six water treatments from three of the contaminated groundwater plume monitoring wells. Treatments included undiluted well water containing the constituents of concern; well water containing high salinity levels (above 2.0mS); and several dilutions of each. Three water treatments were tested in the second pilot study, high, low, and deionized water. The high and low water treatments were based on historically recorded high levels of contamination in the plume water. Trees were evaluated monthly for possible health affects of the constituents of concern. Monthly height, trunk diameter, and foliage visual ratings were taken. Initial and final tissue (root and shoot) and soil samples were collected and analyzed for the potential presence and concentrations of the constituents of concern in the tissue and potting media. Monthly water input and discharge samples were collected and analyzed for the constituents of concern. Results from the pilot studies indicated that both the *Salix nigra* and *Taxodium distichum* species were acceptable phytoremediation choices. However, *Taxodium distichum* was selected for the full scale planting

over the groundwater plume because it was tolerant of the contaminated water treatments and salinity levels present in the groundwater. Additionally, *Taxodium distichum* was a low maintenance tree with a conical form that complied with security restrictions at the chemical facility.

CHAPTER 1

INTRODUCTION

INTRODUCTION

Contaminated Areas

Chemical spills are indicative problems of chemical manufacturing companies. The environmental hazards associated with chemical manufacturing companies may have a potential health affect on citizens who reside near these facilities. Recent studies indicate that human and animal environmental exposure leads to severe health risks (Cristaldi et al., 1991; Boischio and Henshel, 1996; Valberg et al., 1997; and Talmage et al., 1999). Despite the health risks, chemical manufacturing companies create a large number of jobs, which promote economic stability to the areas in which they are located.

Louisiana has a large number of oil refineries and chemical companies. The number of oil-refining and chemical-processing plants located along the lower portion of the Mississippi River rose from 126 in 1962 to 196 in 2002 (Colten, 2006). Although chemical plants and oil refineries enhance Louisiana's economic status, environmental regulations must be followed to ensure safety for Louisiana's citizens. All chemical companies are obliged to abide by environmental laws that were established to prevent or remediate chemical spills.

Several organizations have been established to create environmental laws such as the Louisiana Department of Environmental Quality (LDEQ), Environmental Protection Agency (EPA), and the Occupational Safety and Health Association (OSHA). Through the coordinating efforts of the EPA, LDEQ, and OSHA, Louisiana's local citizens and environment are protected from detrimental harm.

This dissertation discusses the contamination of a groundwater plume in Louisiana. The contaminants of concern (COCs) are semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs). VOCs generally have high vapor pressure, low water solubility, and low molecular weight properties (USGS, 2006). SVOCs have lower vapor pressures than VOCs.

Both can occur naturally or derive from man-made products. Phytoremediation of organic compounds is different than heavy metals because "organic pollutants can be chemically degraded and mineralized into harmless biological compounds, distinguishing them from elemental pollutants" (Cobbett and Meagher, 2002).

Phytoremediation and Traditional Remediation Methods

Several methods are historically used to remediate contaminated areas. Traditional methods of remediation include dig and haul, pump and treat, and soil venting and sparging. These traditional approaches can actually harm the environment. Dig and haul is an invasive method that severely disturbs the natural environment. Stripping a contaminated area removes harmful chemicals but may also remove valuable microorganisms that aid plant growth and biodegradation (Siddiqui, 2004). Without microorganisms in the soil, native vegetation growing on contaminated sites will take a longer period of time to establish.

Phytoremediation is defined as "the use of plants and plant processes to remove, degrade, or render harmless hazardous materials present in the soil or groundwater" (University of Georgia, 1999); and is the name given to a set of technologies that use plants to remediate contaminated sites through contaminant removal, degradation or stabilization (ITRC, 1999). The broad term phytoremediation was first coined in 1991 (McCutcheon, 2003). Eighteen Superfund sites in the United States have implemented phytoremediation as a component of the remediation remedy (Kovalick, 2005). Since 2001, the International Journal of Phytoremediation has been published quarterly (Van Epps, 2006). Phytoremediation is an *in-situ* method of remediation that has been given some attention but warrants further studies. Phytoremediation has been noted as an environmentally friendly alternative to traditional methods like capping, excavation, and soil roasting (Cobbett and Meagher, 2002). Phytoremediation, a non-traditional practice, may be

more efficient and cost-effective when compared with traditional methods (U.S. Environmental Protection Agency, 2001).

The costs associated with remediation can become large. Phytoremediation is comparatively equal to or less expensive to traditional remediation methods. Schnoor *et al.* (1995) estimated that phytoremediation typically costs between 10 to 50% as much as other traditional remediation methods. This same report gave an estimated $10,000 per acre for planting costs with monitoring costs similar to other means of remediation. The US EPA wrote a report comparing the costs of phytoremediation with other remediation technologies. After reviewing several studies, the US EPA (1998) reported that the estimated costs for remediation of metals is 80 dollars per cubic yard for phytoremediation and approximately 250 dollars per cubic yard for other technologies (Black, 1995). The US EPA also reported that estimated costs of petroleum hydrocarbon contaminated sites were 70,000 dollars for phytoremediation technologies and 850,000 dollars for other technologies (Jipson, 1996). In this same EPA study, Plummer (1997) stated that estimated costs of ten acres of land contaminated with lead would require approximately 500,000 dollars for phytoremediation or 12 million dollars for other technologies. Erickson, (2006) stated that phytoremediation is a relatively inexpensive method of contaminant removal for the reason that plants use the sun's light as a source of energy through the process of photosynthesis. Plants have long been known to reduce environmental contamination.

Phytoremediation has several advantages and disadvantages when compared with traditional remediation methods. Advantages include a perception by the general public as a more environmentally friendly approach to remediation; in situ application of remediation: there is no need for off site removal of contaminants; no destructive impact on soil and soil fertility; the newly planted vegetation can restore and even prevent erosion of the contaminated site

(Pivetz, 2001). The disadvantages of phytoremediation include the following; phytoremediation is limited by the root depth of plants; longer periods of time to remove or degrade the contaminants; if plant matter must be removed form the site disposal methods would need to be addressed; if the contaminated substance is water, phytoremediation may slow in dormancy periods when plants use less water; phytoremediation may require the use of greater land space that may interfere with land use activities (Pivetz, 2001). Finally, the need for additional phytoremediation research must be continued before it becomes a widespread method of remediation.

Phytoremediation Mechanisms

Similar to microorganisms, plants have an important role in sustaining and restoring environments. There are four potential mechanisms of organic contaminant phytoremediation by plants; including 1.Direct uptake, accumulation and metabolism of contaminants within plant tissues. 2. Volatilization of organic compounds through plant leaves. 3. Plant release of exudates that stimulate microbial activity and biochemical transformations within the soil. 4. The enhancement of mineralization between the roots and soil because of the presence of particular fungi (Schnoor *et al.*, 1995).

More specifically, phytoremediation that takes place within plants occurs as pollutants are transformed by oxidation or reduction of chemical compounds under the catalysis of cytochrome P-450, monooxygenases, peroxidases, peroxygenases, and others (Ma *et al.*, 2004). After transformation is complete, conjugation begins. During conjugation, sugars, glutathione, and other functional groups have the potential to covalently bond to the transformed pollutant, depending on molecular structures and active sites (Ma *et al.*, 2004). The U.S. EPA Phytoremediation Resource Guide (1999) defines six phytoremediation mechanisms;

phytoaccumulation, phytodegradation, phytostabilisation, phytovolatilization, rhizodegradation, and rhizofiltration.

This study presumes phytostabilisation, rhizodegradation, and hydraulic control to be the hypothesized mechanisms of contaminant removal or control of the COC's in the closed and capped impoundment area plume, along with monitored natural attenuation (MNA). MNA refers to relying on natural attenuation processes to achieve site-specific remedial objectives.

The groundwater plume of concern is located ten to twenty-two feet below ground surface, therefore six tree species (between two pilot studies) were chosen as potential remediators because of their deep taproot structure. A deep tap root system would potentially allow the roots to penetrate the contaminated area. Plants that use large amounts of water and sunlight are the most appropriate for soil and groundwater remediation by phytoremediation (Conger, 2003). Plants that use large amounts of water are termed phreatophytic vegetation; these plants are suitable for phytoremediation because of their high water use rates and fast growth (Gatliff, 1994). The alternative hypothesis is that the selected tree species will degrade the contaminants through phytostabilisation and rhizodegradation; therefore, it is pertinent to understand how water is translocated through the roots and into a tree.

The initial step in organic contaminant translocation into a plant is sorption onto the plant's roots. Organic chemicals in groundwater or soil water may bind to the root's cell wall. The lipid bi-layer of the plant membranes is capable of binding hydrophobic organic chemicals (Dietz and Schnoor, 2001). Water moves from a tree's roots to the stem and leaves through xylem tissue. Xylem tissue is primarily constructed of tracheary elements, xylem fibers, and parenchyma cells. Tracheary cells are a plant's cells most concerned with water translocation within a plant (Devlin, 1969). Tracheids have border pits that are structures that allow water to pass from one tracheid to the next. In some older vessel elements, there are no border walls, and

water can pass directly from one cell to the next, this is the xylem duct (Devlin, 1969). The xylem parenchyma cells are found throughout the wood of a plant. The function of these cells is to store food and enable the sideways transport of both water and nutrients throughout the plant tissue. Water must first enter the tree before moving within the xylem tissue throughout the tree. The root hair zone is the region where most water enters the plant. Water can also enter the root through epidermal cells near the root hair zone. Water then moves through the cortex tissue across the endodermis and pericycle, entering the xylem tissue. This movement occurs through passive transport or osmosis (Devlin, 1969). Several factors influence the absorption of water into the roots. The factors are soil temperature, osmotic pressure of the soil solution, aeration of soil, and availability of soil water. Soils with lower temperatures slow the movement of water translocation into plant. If the osmotic pressure of the soil is greater than that of the root, water will be pulled out of the plant. Roots can grow more easily in aerated soil; therefore plants growing in aerated soils have a larger root mass and can absorb more water than plants growing in poorly aerated soils. The availability of soil water affects the ability of water to be absorbed within the plant. It is hypothesized that some pollutants can be translocated into a tree as water is absorbed. However, a contaminant's physiological properties have an effect on the translocation of a contaminant into a tree.

A good chemical example of physiological properties affecting a chemicals ability to move into a plant is Methyl tert-butyl ether (MTBE). MTBE, an oxygenate, added to gasoline mixtures to improve combustion and reduce carbon monoxide emissions. The US Geological Survey (USGS) found that MTBE was the second highest concentration in groundwater of all volatile organic compounds (Squillance *et al.*, 1996). To find a solution to this problem, Ma *et al.*, (2004) conducted a hydroponic lab study to determine MTBE storage in hybrid poplar cuttings after uptake and its potential to volatilize from poplar tree stems. Results of the

partitioning coefficients of MTBE were as follows, air: leaves 0.0590±0.0092, air: cuttings 0.0585±0.0042, air: roots 0.1208± 0.0143, and water cuttings 0.0048± 0.0010. The partitioning of air to roots was much stronger than that of air to leaves or air to cuttings, Ma *et al.*(2004) supposed that the "relatively low partitioning coefficients are in agreement with the physiochemical properties of MTBE, predominantly the high vapor pressure and water solubility and low Henry's law constant and octanol water partitioning coefficient". The vapor pressure of MTBE is 270hPa at 20ºC. The water solubility of MTBE is 42g/L. Compared to MTBE, cumene's vapor pressure is 8mm Hg @ 20ºC and has water solubility that is listed as insoluble (Matheson Tri Gas, 2007). MTBE has a low Henry's law constant of 65.4 $Pa/m^3/mol$ and a log K_{ow} of 1.06 (European fuel oxygenates association, 2007) which are also low compared to cumene with a Henry law constant of 0.0097atm -m^3/mol and octanol water partitioning coefficient of 3.66 (Ontario Ministry of the Environment, 2001). All of these physiological properties indicate that cumene, unlike MTBE, will not volatilize from plant tissue if taken up by a tree. Ma *et al.*, (2004) concluded that the majority of MTBE taken up by plants was volatilized into the atmosphere while only a small portion remained within the plant biomass, and more specifically in old growth stems. 4-Cumylphenol has a vapor pressure of 2.28 x 10^{-5}mm at 25˚C (0.0030Pa) and water solubility of 43.27mg/L at 25˚C (Schenectady International, 2007). 4-Cumylphenol is also unlikely to evaporate from leaves.

The Interstate Technology and Regulatory Council (ITRC) decision tree, a document that helps determine the usability of phytoremediation techniques for specific purposes, uses the log K_{ow} of the COC to indicate the trees ability to remove the contaminant from groundwater. The "octanol-water partition coefficient (K_{ow}) is a measurement of how a chemical is distributed at equilibrium between octanol and water. It is an important parameter often used in the assessment of environmental fate and transport for organic chemicals" (Miller, 2006). The ITRC decision

tree indicates that organic constituents with a log K_{ow} of 1.0-3.5 are able to be translocated within the plant and are considered moderately hydrophobic. Constituents with log K_{ow} values above this critical range are not expected to be translocated into the plant because they are tightly bound to the soil and roots. Chemicals with a log K_{ow} less than 1.0 are hydrophilic and are not adsorbed to a plants roots nor taken up through active transport (Briggs *et al.*, 1982). Thus contaminants with a log K_{ow} above or below this range would benefit from rhizodegradation. According to the ITRC decision tree, translocation of α, α-DMBA will occur as its log K_{ow} is 1.95, whereas, cumene and 4-cumlyphenol will not pass the root membrane since their log K_{ow} values are 3.66 and 4.12 respectively (Schenectady International, 2007).

Using Burken and Schnoor's "Distribution and Volatilization of Organic Compounds Following Uptake by Hybrid Poplar Tree" researchers confirmed that phenol will be taken up by plants and that it remains primarily in the roots and bottom portion of the stem (Burken *et al.*, 1999). The octanol water partition coefficient also helps determine the applicable portions of the tree to sample when completing final tissue samples for COC's and their metabolites. Those COC's with higher log K_{ow}'s (3.0 and above), if absorbed in or on a plants roots will not likely leave the root tissue, whereas COC's that are within the 1.0-3.0 log K_{ow} range may pass into the roots and move through the xylem up into the leaves, each contaminant being specific.

Phytoremediation along with monitored natural attenuation (MNA) have been selected to remediate the closed and capped impoundment area plume water. These naturally occurring processes include advection, hydrodynamic dispersion, adsorption, biodegradation, volatilization, and radioactive decay (PSI, 2003). Some of these processes eliminate contaminants, while other processes reduce contaminant mobility or concentrations, thus transforming the contaminants into less toxic compounds (PSI, 2003). The three principals of natural attenuation processes include: 1) contaminant transformation towards less toxic forms via

processes like biodegradation or abiotic conversion; 2) reduction of contamination concentrations leading to a reduction of exposure risks; and 3) "monitored natural attenuation" (MNA) provides detailed and scientific evaluation of the congruence of the cleanup objectives (protection of human health and of the environment) with the progress of the remediation (PSI, 2003). The implementation of MNA alone may result in longer remediation times than Georgia-Pacific preferred. Therefore, this study proposes that MNA be coupled with phytoremediation efforts. The combination can be cost-effective because residual contaminants may be rapidly removed using trees that act as an enhancement of an in situ degradation mechanisms for contaminated groundwater.

Site Information

A closed and capped one-acre surface impoundment is located on the property of Georgia Gulf Chemicals & Vinyl's, LLC near Plaquemine, Louisiana (Figure A-1, Appendix). The impoundment was used between the years of 1975 to 1981 as a waste disposal area. Waste in the impoundment originally came from a train wreck carrying phenolic compounds and waste products from the facility in Plaquemine, LA.

Georgia-Pacific Corporation retained liability for this closed surface impoundment after sale of the property to Georgia Gulf. Although soil within the closed and capped surface impoundment had been remediated during closure in 1989, a contaminated groundwater plume of cumene and 4-cumylphenol remains along the down gradient (eastern) boundary of the closed surface impoundment. Georgia-Pacific submitted the Corrective Action Plan (CAP) for the closed surface impoundment facility prepared by Professional Service Industries, Inc. (PSI) to the Louisiana Department of Environmental Quality (DEQ) in 2003. The CAP was submitted to achieve compliance with the hazardous waste facility permit issued by the DEQ with regard to the water quality conditions in the uppermost groundwater zone present at approximately 10 to

22 feet below ground surface. The CAP design included a component involving phytoremediation. In 2005 the DEQ stated that a "pilot study is necessary to demonstrate the technical viability of Georgia-Pacific's proposed CAP" since no information is available regarding phytoremediation of the specific constituents of concern (COC's) in groundwater at the facility as proposed by Georgia-Pacific. Georgia-Pacific submitted the required work plan for a "Phytotoxicity Study" to determine the viability of candidate tree species, which was approved by the DEQ in February 2006.

The COC's of primary interest include cumene (isopropyl benzene), α, α-dimethylbenzyl alcohol (α, α-DMBA), total phenols and 4-cumylphenol, which are present at notable concentrations in the groundwater plume. The maximum values for each COC during the 2005 and 2007 compliance monitoring periods are presented in Table 1. Cumene and 4-cumylphenol are the only COC's that currently exhibit concentrations exceeding current standards of 0.066mg/L for cumene and 0.180mg/L for 4-cumylphenol defined in the hazardous waste facility permit issued by the LDEQ; therefore the study centered on these two contaminants.

Table 1. Maximum Concentrations of Constituents of Concern in the Groundwater Plume in 2005

COC	Maximum Concentration (mg/L) 2005	Maximum Concentration (mg/L) 2007
Cumene	0.483	0.129
α, α-Dimethylbenzyl alcohol	0.0416	0.0463
Total phenols	0.071	0.067
4-Cumylphenol	4.400	2.640

Table values provided by PSI.

The first pilot study's results indicated that *Taxodium distichum* was the optimum tree species for phytoremediation of the contaminants in the plume water. However, Georgia-Pacific funded a second pilot study allowing minor modifications to be made to optimize the results of the phytotoxicity study. The second study was initiated in October of 2007 and ended in June of 2008. Study modifications included using elevated concentrations of cumene and 4-cumylphenol

in the hydroponic system, adding *Populus deltoides* (cottonwood) to the tested tree species, and adding a water usage study by individual species. Results from the second pilot study indicated that *Salix nigra*, and *Taxodium distichum* were acceptable candidates for phytoremediation of the constituents of concern. Because of tolerance of chemicals and salinity and complying with security restrictions, *Taxodium distichum* was the selected tree species for full scale planting of the groundwater plume.

Research Questions

The uppermost groundwater zone, Stratum III groundwater, has been impacted by the migration of organic compounds previously disposed in the closed and capped impoundment area. The objectives in the Corrective Action Plan (CAP) prepared by PSI; were 1) to ensure that groundwater meets applicable water quality standards within a reasonable time period; 2) to ensure minimal future migration of groundwater contamination; 3) and to ensure that future risks to public health, safety, and welfare, or the environment do not occur.

To ensure that the objectives of the CAP are met, Georgia-Pacific funded two phytoremediation pilot studies. Both pilot studies were conducted at Georgia Gulf in June 2006 to March 2007 and October 2007 to June 2008. The main research questions were; 1) Will the selected tree species survive contact with the contaminated groundwater? 2) Will the selected tree species create a hydraulic barrier keeping the contaminated groundwater plume on Georgia Gulf property? 3) Will the selected tree species affect the COCs through the phytoremediation mechanisms phytostabilisation, rhizodegradation, or hydraulic control?

The goals of the phytoremediation approach to remediation of the groundwater plume will not be met unless the proposed tree species penetrate the Stratum III groundwater zone and survive contact with the contaminated groundwater. Therefore six tree species were chosen for the greenhouse pilot studies. The select tree species are: *Salix nigra,* black willow; *Populus*

deltoides, cottonwood; *Juniperus virginiana,* eastern red cedar, *Quercus nigra,* water oak; *Taxodium distichum,* bald cypress; and *Pinus glabra,* spruce pine. The tree species were chosen for their deep root structures, with the exception of the black willow, which was chosen because it has been successful in other phytoremediation projects (Conger, 2003). Additionally, these tree species generally require large amounts of water, lending them to be considered ideal candidates for hydraulic control of the plume. There are two possible outcomes of this study, one is that cumene and 4-cumylphenol will adsorb onto the trees roots, bind tightly in the soil matrix around the roots and begin to degrade by means of rhizodegradation and phytodegradation. A second hypothesis is that the trees will not phytoremediate cumene and 4-cumylphenol, but will create a hydraulic barrier keeping the contaminated groundwater plume within the chemical facilities boundaries.

Organization of the Dissertation

The dissertation paper covers 3 separate studies. The first study was a greenhouse study replicated twice over two consecutive nine month periods. The second study was a toxicity study that looked at adverse effects on seed germination and radical length of higher order plants in the presence of cumene and 4-cumylphenol contaminated soil water. The third study was a preliminary fate and translocation study that looked at the movement and metabolites of cumene and 4-cumylphenol in black willow cuttings.

Chapter 2 focuses on background information on the two principal constituents of concern, cumene and 4-cumylphenol. This chapter gives information on the toxicity of the chemicals. Tentatively Identified Chemical (TIC) information is also given in chapter 2. TIC information from soil and tissue samples aided in identifying potential unknown metabolites of the COC's. Although no TICs found in the soil or plant tissue amounted to significant metabolites. Chapter 3 gives background information on the contaminated groundwater plume. It

also details all materials and methods used in the greenhouse studies to evaluate phytoremediation as a possible method for remediation of the COCs. Chapters 4 and 5 present the results from the two greenhouse studies. The results in these chapters are categorized by environmental conditions, plant quality, water, soil, tissue, and sludge data. Chapter 6 provides the overall conclusions from the two greenhouse studies. The full scale planting over the contaminated groundwater plume is also described in this chapter. Chapter 7 contains all of the toxicity study information. It is organized into several sections including an introduction, materials and methods, results and conclusions section. Chapter 8 contains all of the information from the fate and translocation study. It is organized similarly to Chapter 7, containing an introduction, materials and methods, results, and conclusions section. Chapter 9 provides overall conclusions from all 3 studies. Future recommendations for studying phytoremediation of cumene and 4-cumylphenol are made in this chapter.

CHAPTER 2

LITERATURE REVIEW

LITERATURE REVIEW

"Phytoremediation is the engineered use of green plants to remove, contain, or render harmless environmental contaminants such as heavy metals, trace elements, organic compounds, and radioactive compounds in soil or water" (Hinchman, 1998). Plants are able to remediate hazardous organic substances through processes such as uptake, accumulation, metabolism, and microbial transformation (Shimp *et al.*, 1993). Using phytoremediation as a means to clean up contamination was begun as early as the 1970's. However, phytoremediation became a more widely proposed remediation method in the 1980's and early 1990's (Phillips, 2006). Some of the first phytoremediation initiatives included efforts to remediate contaminants such as pesticides, excess fertilizers, and wastewater.

As early as 1922, I.L. Baldwin studied the affects of crude petroleum on plants. In the early 1980's Anderson, *et al.*, 1983 and Zieve and Peterson (1984) investigated the uptake of metals into plants. Specifically these researchers were looking at Selenium. Boersma, and co-workers (1988) designed a model for the potential uptake of organic chemicals in plants. As research continued, phytoremediation projects began to encompass more specific research including using radio labeled chemicals as tracers through plant systems. Burken (1996, 1999) studied the uptake and pathways of organic contaminants through poplar trees. However, because of limited research, the general understanding of the basic plant processes that remediate organic chemicals falls behind our understanding of microbial degradation of organics. It is difficult to separate the interaction of plant processes and microbial degradation of chemicals (Raskin, 2006).

Phytoremediation research has not been conducted on the remediation of cumene and 4-cumylphenol, the constituents of concern for this research project. Therefore, this project will explore the plausibility of using several mechanisms of phytoremediation to remove, render

harmless, or contain the cumene and 4-cumylphenol in the closed and capped impoundment area groundwater plume on Georgia Gulf's property.

Cumene

Cumene, (C_9H_{12}), is an aromatic hydrocarbon. Its CAS number is 98-82-8. Cumene is used to manufacture several chemicals such as phenol and acetone (USEPA, 1998). In the early 1990's, cumene was in the top 50 chemicals made in the United States. Approximately 4.5 billion pounds of cumene were produced annually (Reisch, 1993). It is commonly found as a clear liquid, is flammable, and has a strong odor. According to Spectrum Laboratories, cumene's odor can be perceived by humans at 0.06mg/cu m or 0.012ppm. It can be detected in the air at 0.008ppm and can be recognized as cumene and not another chemical at a concentration of 0.047ppm. Cumene's molecular weight is 120.19 (Spectrum Laboratories, 2006). The log K_{ow} or octanol water partition coefficient of cumene is 3.66 (Phillip, H., 1997). The octanol-water partition coefficient has been used to determine if a particular contaminant has the potential to translocate into a plant. The log K_{ow}, can also determine the fate of a contaminant. Based on previous work by Briggs *et al.*, 1982 and Shone *et al.*, 1972 chemicals with a log K_{ow} <1.8 will not pass through epidermal root cells, while chemicals with a log K_{ow} >1.8 will enter the root tissue. Chemicals with a log K_{ow} >1.8 would not be able to enter into the xylem. Since movement into the xylem would not occur, the chemical would not be able to enter the stem or leaves of a plant. The log K_{ow} corresponds to the transpiration stream concentration factor (TSCF). The TSCF is calculated by the concentration in the transpiration stream divided by the bulk solution concentration in contact with the root tissues (Burken *et al.*, 1998). Because of its log K_{ow} it is projected that cumene may pass through the endodermis of tree root cells but will remain in the roots of the tree and not translocate to other tissue. The log K_{ow} is not the sole factor for determining uptake of chemicals by plants. The US EPA, 1998 stated that cumene is expected to

absorb to soil and to have the ability to biodegrade in both soil and water. The plume is 10-20 feet below ground surface and characterized as an anaerobic environment. Cumene's half-life in surface water has been reported at 5.79hr with an evaporative loss at 25°C in 1m water depth (Mackay and Leinonen, 1974). However a separate study reported that cumene biodegrades to carbon dioxide in aerobic aquatic environments and mineralizes with a half-life of approximately 34.6days (Williams et al., 1993). Glickman and colleagues (1995) reported that volatilization plus biodegradation equate to a half-life of 2.5days for cumene. The deficiency of oxygen in the groundwater plume of concern in this dissertation is probably contributing to the lack of degradation of cumene in the contaminated plume water.

Toxicity

Several studies have been conducted accessing the toxicity of cumene. Senczuk et al., (1976) conducted a study exposing only human heads (95 male, 5 female) to three concentrations of cumene vapors for 8 hours a day over a 10 day time period. By analyzing exhaled breath samples the researchers determined the total amount of cumene absorbed was twice as high in males as females. Mean retention time of cumene in the human system was estimated to be 50%. Sato *et al.*, 1987, determined that metabolism by cytochrome P-450 of cumene takes place in both the hepatic and extra hepatic tissues. They found that a secondary alcohol, 2-phenyl-2-propanol (synonym α, α DMBA) was the principal metabolite. EPA classifies cumene as a class D carcinogen. Class D means that there is insufficient data to support that the chemical is cancer causing.

4-Cumylphenol

4-Cumylphenol ($C_{15}H_{16}O$) is an aromatic hydrocarbon. Its CAS number is 599-64-4. 4-Cumylphenol is used as a precursor chemical to producing rubber and plastic products. It is commonly found as a cream-colored solid material and is manufactured by combining alpha

methyl styrene and phenol (EPA, 2001). It has a strong odor. The molecular weight of 4-cumylphenol is 212.28g/mol. The log K_{ow} of 4-cumylphenol is 4.1 allowing this chemical to pass through the root membrane but not enter the xylem.

Toxicity

Toxicity information on 4-cumylphenol is scarce. The MSDS lists 4-cumylphenol as a skin, eye and respiratory irritant. Several 4-cumylphenol toxicity tests were preformed by both the Safety Research Institute for Chemical Compounds Co., Ltd. and Hatano Research Institute, Food and Drug Safety Center located in Japan. Data presented in an abstract by The Safety Research Institute for Chemical Compounds and Hatano Research Institute, Food and Drug Safety Center in 2009 reported an oral toxicity test gave a LD_{50} value of 2000mg/kg or more for male and female rats. At 1500mg/kg of 4-cumylphenol in olive oil rats experienced weight loss bile duct problems, and foreign black matter in urine samples. These same groups preformed a reverse mutation test on bacteria and found that 4-cumylphenol was non-mutagenic. The genotoxicity of 4-cumylphenol was also studied using a chromosomal aberration test on Chinese hamster lung cells. 4-Cumylphenol did not cause any structural chromosomal abberations or polyploidy at any of the tested doses.

The structure of 4-cumylphenol is similar to Bisphenol A, which is a known endocrine disruptor. The only difference between 4-cumylphenol and Bisphenol A is that Bisphenol A has an additional alcohol (OH) attached to its second benzene ring. Matsushima, *et al*., 2008 conducted a study looking at the potential of both Bisphenol A and 4-cumylphenol to bind to a human estrogen related receptor ERRγ. ERRγ is expressed in mammalian fetal brains and placenta and may have important contributions to the health of newborns. The receptor binding affinity of 4-cumylphenol and Bisphenol A was very similar. Bisphenol A had a binding affinity of 13.1+ or – 2.34 while 4-cumylphenol had a binding affinity of 13.9+ or – 1.98 IC_{50} nM.

Matsushima *et al*., 2008 found that it was the A ring of the phenol-hydroxyl group that allows Bisphenol A and 4-cumylphenol to bind to ERRγ. More studies need to be completed to find out the effects of these chemicals binding to this particular receptor site.

Biggers et al., 2004 found that four alkylphenols, including 4-cumylphenol (synonym 4-dimethylbenzyl –phenol) were found in American lobster tissue and marine sediments. The paper notes that alkylphenols in high concentrations can cause mortality in lobsters and in low concentrations can have endocrine disrupting effects (Biggers *et al*., 2004). This article did not note if the alkylphenols found in the lobster tissue in this case had any endocrine disrupting effects.

Tentatively Identified Compounds (TICs)

Determining the identities of possible metabolites of cumene and 4-cumylphenol was essential to understanding the Tentatively Identified Compound (TIC) data from Pace Analytical lab. PSI and LSU obtained information from Georgia Gulf technical staff regarding potential metabolites for these two chemicals under aerobic conditions in soil, since there is very little information available from literature on these chemicals.

Metabolites of cumene breakdown as per discussion with environmental engineers at Georgia Gulf are believed to be:

Cumene → α, α-DMBA → α-Methylstyrene + Water

Cumene → Acetophenone + Methanol

Methanol → Formaldehyde → Formic acid → Carbon dioxide + Water

Metabolites of 4-cumylphenol breakdown are believed to be:

4-cumylphenol → α-Methylstyrene + Phenol

Phenol was the primary COC investigated during bench scale and field pilot studies for the soil remediation for this project site performed in the late 1980's, and was documented to

rapidly break down (mineralize) to harmless byproducts in aerobic soil conditions (with no plants). All of the other project COC's, including cumene, α-methylstyrene, acetophenone and 4-cumylphenol, were also documented to mineralize during these previous pilot studies (Georgia-Pacific Corporation *et al*, 1987). They are detected in the well water because they are in anaerobic conditions at 10-22ft below ground surface.

Based on chemical make-up of cumene and 4-cumylphenol and proposed pathways, it is not likely that these two constituents of concern will enter a tree's roots, and translocates into the xylem. Therefore the hypothesis of this study is that cumene and 4-cumylphenol will not translocates into the stem tissue of the selected tree species. It is hypothesized that cumene and 4-cumylphenol will adsorb onto the trees roots, bind tightly in the soil matrix around the roots and begin to degrade by means of rhizodegradation and phytodegradation. A second hypothesis is that the trees will not phytoremediate cumene and 4-cumylphenol, but will create a hydraulic barrier keeping the contaminated groundwater plume within the chemical facilities boundaries.

CHAPTER 3

MATERIALS AND METHODS

MATERIALS AND METHODS

Site Description

The capped off impoundment area studied in this project is located on the east side of the Georgia Gulf plant in Plaquemine, Louisiana (Appendix). It was used for many years as a chemical impoundment. A greenhouse structure was assembled in June of 2006 directly east of the impoundment area (Appendix). This location was chosen for easy accessibility to the Stratum III groundwater monitoring wells see the Appendix for a map of the monitoring wells. The monitoring wells are located around and over the groundwater plume. Monitoring wells NS2, NS6 and NS8 (NS is short for North/South) were selected as the first pilot study's source of treatment water. Wells NS2 and NS8 have elevated levels of cumene and 4-cumylphenol while well NS6 has elevated levels of NaCl.

A pilot greenhouse study was initiated in June of 2006 to determine an optimum tree species for tree survival, contaminant removal, and hydraulic control of the contaminated groundwater plume. A hydroponic trough system was used to mimic a tree's root structure entering the groundwater plume. To develop a method for water uptake in the trough system, a short experiment was conducted to determine the appropriate material for wicks to serve as conduits for the water to the trees until the root systems grew out of the pots and into the treatment water.

MATERIALS

Wick Pilot Experiment

A one-week pilot study, initiated on January 4, 2006, was conducted to determine the optimum wick material, cotton verses nylon, and placement in pots. Cotton rope with a 0.25in (0.635cm) diameter and remnant material strips were cut into 43cm lengths. *Callistemon citrinus,* bottlebrush plant, was chosen for the wick experiment because it was an available

woody ornamental species. The trees to be used in the pilot study were not available at this time. Two cotton ropes or two remnant strips (a nylon fabric used in the whole nursery industry) were inserted into the side holes or center holes of the 3.79L pots containing bottlebrush plants. Each pot was then watered with 710mL of water to ensure that the soil was moist, as wicking systems work best when the soil is moist. The plants were monitored daily until the eleventh of January, 2006. Using a feel test and visual wilt ratings, the optimum wick material and placement was determined. Results indicated that the 3 remnant material strips located in the side holes kept the potted bottlebrush plants from wilting. However, 4 remnant strips were placed in each pot to ensure adequate water uptake. Therefore 4 remnant material strips approximately 33cm long were placed in the side hole of each pot used in the pilot study. The wicks used in the hydroponic system did not need to be 43cm because they were excessively long for the inside diameter of the hydroponic troughs. The remnant strips were long enough to extend from the top of the soil line in the pot to the middle of the hydroponic trough. Once it was determined that the wicks would adequately moisten the treatment trees in trade gallon pots, the rest of the hydroponic system was constructed, beginning with the greenhouse.

Greenhouse Description

A greenhouse structure (hoop house), 10m x 20m was built on the Georgia Gulf plant adjacent to the closed and capped impoundment area. The greenhouse had two functions. The first was to house the hydroponic system and the second was to keep rainwater from diluting the treatment water. A polyurethane roof and sidewalls were added to the greenhouse structure using poly-locks to secure the plastic to the metal structure. A shade cloth covered the roof to lower overall temperature in the greenhouse. The roof extended to the sidewalls of the greenhouse. The sidewalls were approximately 1.40m above ground level surface. End walls covered with a polyurethane plastic were then built to protect the inside of the greenhouse from wind and rain.

Two 2.67m doorways were located on either end of the greenhouse structure for easy access into the greenhouse. Because electricity was not available for operating fans or a cooling system, the bottom 1.4m of side walls and end walls were not covered in plastic, allowing air movement throughout the greenhouse. After the greenhouse was built construction of the troughs used to hold the treatment trees and water treatments began. Together the troughs and the gravity feed irrigation combined to form the hydroponic system.

Hydroponic Water System

Schedule forty PVC pipe was used as a trough to contain the trees. The trough was approximately 15.24cm in diameter. Each trough was cut to 2m in length with five 14cm holes cut on 30.48cm centers. The holes were cut using a hole saw attached to a portable drill press. Two additional 2.54cm holes were cut into the top and bottom of the trough. The top hole was plugged with a rubber cork later to be used as a water level monitoring hole when filling the trough. The bottom hole was fitted with a flush saddle to ensure 100% drainage. PVC primer, PVC glue, and silicon were used to attach the saddle and end caps. One of the end caps was then fitted with a 1.27cm male insert to allow water to fill the troughs from the attached Poly-Drip™ poly-tubing. The end cap with the 1.27cm male insert was connected with a 1.27cm poly tube that was then connected using a 90˚ elbow and a 2.54cm T to a 2.54cm poly-tube that connected with one of the six 208.20L tanks that served as the main feeder tanks.

The feeder tanks sat on elevated tables outside of the south end of the greenhouse. It was necessary to have elevated tables to ensure that the gravity feed irrigation system had enough force to transport water from the south to north end of the greenhouse. All troughs sat on wood pallets varying in height, which further allowed gravity to move water to each trough. Each of the six 208.20L tanks held one of the six water treatments (3 water treatments in the second pilot study).

Valves regulated flow of treatment water from the main feeder tanks (208.20L tanks) through the poly-tubes to the troughs. Additional, valves were located on the input side of each trough (Male 1.27cm insert in the end cap) to regulate treatment water movement into each individual trough. Valves were also placed on the drainage side of troughs to regulate drainage from individual troughs. All drains were connected with 2.54cm poly-tube to a hard PVC line, which transferred the discharge water into a submerged sump tank.

The sump tank was located on the north end of the greenhouse, opposite from the 208.20L feeder tanks. A battery-operated sump pump was used to remove water from the submerged sump tank. The discharge water was then transferred on a large trailer tank to Georgia Gulf wastewater treatment facilities.

DI water was added to the hydroponic systems several times to locate and repair leaks in the system. Once all leaks were repaired, the treatment trees were brought to the greenhouse and placed into the troughs in a complete randomized block design.

Selected Tree Species

Two of the most widely used tree species in phytoremediation projects are the *Salix nigra,* black willow and *Populus deltoids,* cottonwood. As widely used as these two species are, it is critical that research on many tree species occur because remediation of chemicals can be species dependent. For instance, Fischerová and colleagues (2006) found that *Salix sp*. and *Populus sp*. were both proven phytoremediators of arsenic, cadmium, lead, and zinc. The *Salix sp*. was more efficient remediators of arsenic, cadmium, and zinc, while the *Populus sp*. was better at phytoremediation of lead. Based on this knowledge, we choose to study both the *Salix* and *Populus* tree species as well as other tree species for phytoremediation of cumene and 4-cumylphenol contaminated groundwater.

The six trees that were chosen for this project were *Salix nigra,* (black willow), *Juniperus virginiana,* (eastern red cedar), *Pinus glabra* (spruce pine)*, Taxodium distichum* (bald cypress), and *Quercus nigra* (water oak). Cottonwood (*Populus deltoids*) was proposed for usage in the first study. However, because of an insufficient number of seedlings, cottonwood was not used in the first study, but was used in the second study. Only the bald cypress, black willow, and poplar trees were used in the second study. The selected tree species were chosen for their deep root systems and ability to take up large quantities of water.

It is hypothesized that the Black willow will be a successful candidate for phytoremediation of the constituents of concern (COC's). Dimitriou et al. (2006) studied the effects of landfill leachate on five species of *Salix.* The results indicated that the landfill leachate did not improve plant growth similar to fertilizer but did indicate that the willows played an important role in remediation of harmful chemicals from the leachate (Dimitroiu et al., 2006). The study reported that there were close to 30 *Salix* species systems treating landfill sites in Sweden. Another study indicated that willow plantings over landfill caps decreased leachate formation under the cap because of the large amounts of water used and evpotranspirated by the trees (Cureton et al., 1991 and Ettala, 1988). Additional studies indicate that hazardous compounds in leachates could be translocated by willows and or retained within the soil around the willow roots (Aronsson and Perttu, 2001). French and colleagues (2006) demonstrated that *Salix*, *Populus*, and *Alnus* woody species were able to phytoextract and reduce cadmium and zinc contamination in landfills throughout their typical 25 to 30 year life spans. These studies and others have shown that willows are efficient species for phytoremediation of certain chemicals. The previous research leads to the hypothesis that black willows used in this pilot study may serve as successful candidates for the phytoremediation of the COC's.

The hybrid poplar tree is also a popular candidate for phytoremediation projects. Poplar trees have often been chosen for phytoremediation projects because they are a perennial species that is tolerant to high concentrations of organics, are fast growing and can easily be propagated (Paterson and Schnoor, 1992). In a study by Ma in 2004, hybrid poplar trees, specifically the *Poplar deltoids x P. nigra* were able to accumulate methyl tert-butyl ether (MTEB) from water in a lab scale project (Ma, 2004). Using carbon –11 nuclear imaging, Ferrieri and colleagues (2005) found that poplar cuttings were successful translocators of carbon tetrachloride (CCl_4) and were able to metabolize the CCl_4 through carbon fixation in the foliage. The following paragraphs give plant characteristics of the tree species chosen for this dissertation.

Salix nigra

Black willow is a native tree of North America and can be found all throughout the southern states (Odenwald, 2000). It can reach maximum heights of seventy to eighty feet with a maximum width of forty feet (Odenwald, 2000). A major advantage of the black willow is its exploratory water-seeking roots, which indicate its potential for hydraulic control of the contaminants. The limitations of this species are its shallow root system and short life span. The black willow has been used in other phytoremediation projects (Conger, 2003).

Quercus nigra

Water oak can be found on the east coast of the United States from Delaware south towards Florida, and west towards Texas (Odenwald, 2000). The water oak is found in moist upland soils and on the edges of swamps throughout the South (Odenwald, 2000). It can reach heights of one hundred feet and canopies sixty feet wide (Odenwald, 2000). The main advantage of the water oak is its ability to take up large amounts of water through its deep tap root system.

Juniperus virginiana

Eastern red cedar is one of the most widely distributed conifers in North America (Odenwald, 2000). It can survive in poor soils and is noted for its salt tolerance (Odenwald, 2000). The eastern red cedar may reach maximum heights of fifty to one hundred feet and maximum widths of thirty feet (Odenwald, 2000). The eastern red cedar was not only chosen for its root structure but also for its salt tolerance. Salt tolerance is important; as well water in the NS6 well contains salt levels above 2mS.

Taxodium distichum

Bald cypress is a native of North America (Odenwald, 2000). It can grow in a variety of soils ranging from upland to coastal soils (Odenwald, 2000). This tree is known for its ability to survive in water. Its taproot is very long. The cypress is also noted for its knees, which occur in wet environments. The knees are extensions of the roots (Dirr, 1998). Bald cypress can reach a maximum height of one hundred feet tall and a maximum width of sixty feet (Odenwald, 2000).

Populus deltoides

Cottonwood is in the willow family and is noted for being a fast-growing species. It is native to North America and grows throughout the eastern United States. Cottonwoods are tolerant of flooding conditions and conditions where soil is eroded away from the base of the trunk and water fills the void. The roots of cottonwood trees can reach several meters deep in moist soils (Mitchell et al., 2008). Life spans of cottonwoods can reach up to 60 to 200 years.

Pinus glabra

Spruce pine is native to North America, ranging from South Carolina to Louisiana. It is a moderately fast growing tree with a deep taproot (Odenwald, 2000). The spruce pine can tolerate heavier soils than most pine species. It can be found in a range of environments from uplands to areas where flooding is shallow and brief. (Dirr, 1998)

Each of the listed tree species is a suitable candidate for phytoremediation of the constituents of concern at the groundwater of the closed and capped impoundment area. All chosen species, except black willow, have deep taproot systems, which will be helpful in penetrating the Stratum III groundwater plume. All of the chosen tree species are also known for their ability to survive in wet conditions.

Experimental Design

A randomized complete block design was used to set up the hydroponic system inside the greenhouse (Figure 1). In the first pilot study the design consisted of five blocks. Each block included eight troughs. One trough was allocated to each water treatment. However, because the control and 33% NS2 and NS8 water treatments were doubled two troughs per block were allocated to these water treatments. All troughs were randomly assigned within the block. Each of the five tree species were represented in each trough. The trees were given randomized assigned positions within the troughs. Therefore, each block consisted of eight troughs and forty trees.

The experimental design of the second pilot study was similar to the first. However, the greenhouse was divided into two separate studies including a water usage study and the phytoremediation study (Figure 2).

The front half of the greenhouse was designated for the phytoremediation portion of the study. This experiment was set up in a complete randomized block design.

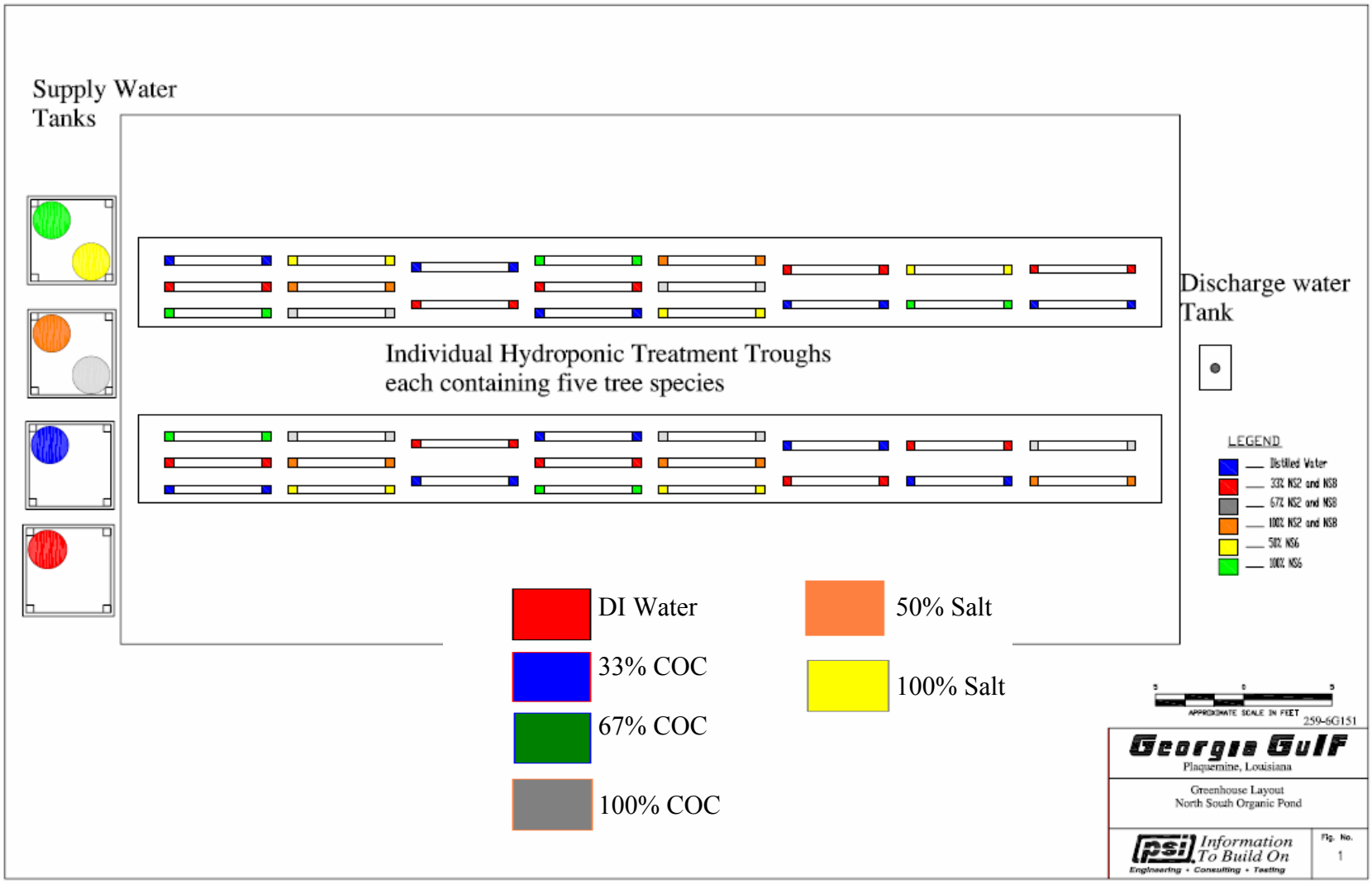

Figure 1. Greenhouse Schematic Pilot Study. Figure provided by PSI

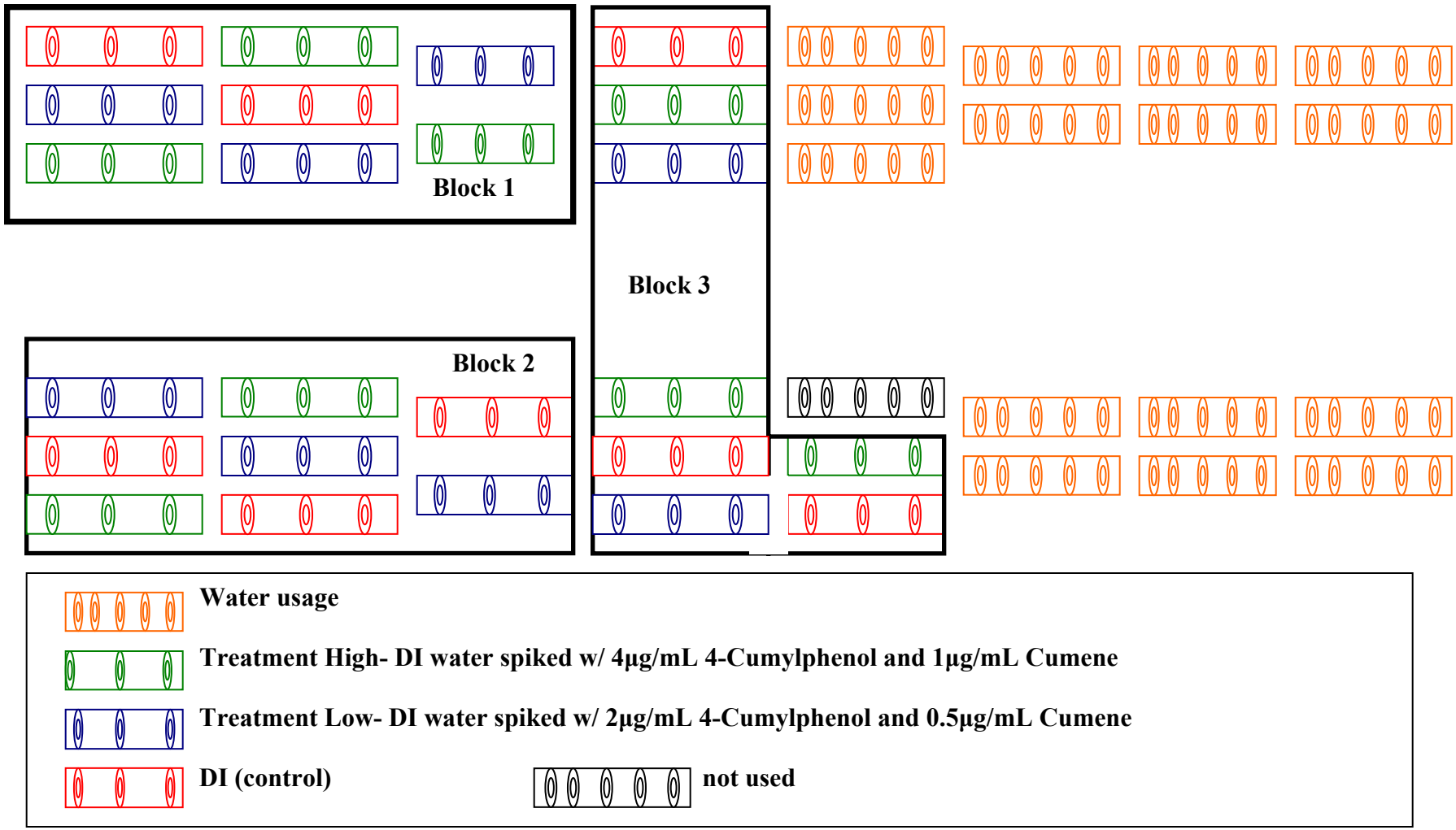

Figure 2. Greenhouse Schematic Pilot Study 2

The phytoremediation portion was divided into three blocks. Within each block were eight troughs. Three trees were placed into each trough. The trough included one tree from each of the tested species (bald cypress, cottonwood and black willow). There were a total of twenty-four troughs, eight troughs per water treatment (high, low, and control). There were a total of seventy-two trees in the phytoremediation portion of the pilot study, twenty-four trees per water treatment and five trees per individual trough in each water treatment.

The back portion of the greenhouse was dedicated to research water uptake by species. This portion of the study was a complete randomized design. There were no blocks. The water study consisted of 15 troughs. Each trough held five trees. Each trough was dedicated to one tree species. There were five tree species studied. The species included; eastern red cedar, cottonwood, black willow, bald cypress, and water oak. De-ionized water was used in this portion of the study. Chemicals were not introduced to the water usage portion of the study.

Media

Trees were grown in FAFARD Red Bag Mix #2 peat-based media. Bark was not added to the media because bark clogs the machines used in soil analysis and makes extracting COC's difficult. However, the bulk density of the media needed to be increased for tree support. Native soil from Baton Rouge, Louisiana was used to amend the soil. Adding native soil gave the media higher bulk density and added micronutrients and microorganisms to the media. Micronutrients are not found in sterile peat mixes used in the horticulture and landscape industry and the levels of microorganisms are low. Microorganisms are useful in remediation because of their ability to aid in the bioremediation of the COC's within the trees rhizosphere. However, identification of microorganisms was not conducted in this study.

The media was mixed into 1 ft^3 bales. Native soil was sieved using a 0.6cm sieve. Twenty-three cubic feet of FAFARD peat and perlite mixture was mixed with 4ft^3 of native soil

(approximately 20 percent native soil). A medium rate of Osmocote (4.53kg) 15-9-12 (N-P-K) (9 months live at 21.1°C) was incorporated into the media. Trees were potted into trade gallon injection mold pots.

Pots

A trade gallon-sized pot was an appropriate sized pot for use in the hydroponic troughs. The pots were injection mold pots, and were smooth on all sides, making them suitable for rubber aprons. Rubber aprons were cut from a 0.3cm butyl rubber. Aprons were cut into one-square foot pieces. A 15cm hole was then cut into the middle of the apron to fit around the diameter of the pot. The aprons were glued to the pots using Fix-all™, a multi-purpose adhesive and sealant. The purpose of the aprons was to prevent evaporation of the water between the seams of the pot and the trough. The rubber aprons were also attached to limit an escape route for any volatilization of chemicals from the seams between the pots and troughs.

METHODS

Both phytotoxicity pilot studies were conducted for nine months. Construction of the greenhouse was completed in June 2006 and the first pilot study was initiated. The first study ended in March 2007. The second pilot study was initiated in October of 2007 and ended in June of 2008. The following paragraphs describe data collected as well as the sampling methods used to analyze the water, soil, and sludge from both greenhouse studies.

Environmental Conditions

Relative Humidity

Relative humidity (RH) was monitored weekly. Relative humidity is an environmental factor that can affect a trees growth. A plant will increase transpiration on low relative humidity, high heat, windy days as opposed to high relative humidity, cool days. Too much transpiration can lead to wilting. Since the trees in study were growing hydroponically, it was better to have

higher relative humidity days. Relative humidity is usually given as a percent. Battery-operated data loggers were used to monitor the relative humidity every 30 min in the greenhouse. The average monthly RH were calculated and reported.

Temperature

Weekly high and low temperatures were collected. Air temperature affects tree growth rate. Optimum growing conditions for trees fall between the temperatures of 70°F (21°C) and 85°F (29°C). A trees thermal death threshold is around 115°F (46°C) (Coder, 1996). Trees must quickly adjust to high temperatures in order to survive the extreme heat. Temperatures were collected every 30 minutes using battery-operated data collectors in the greenhouse. Temperature was also monitored weekly using a high/low mercury thermometer. The average monthly high and low temperatures were calculated and recorded.

Insect and Disease

Weekly greenhouse visits included inspections for disease and insect damage. During the first pilot study a combination of soap and water was sprayed several times to eliminate aphids, spider mites, and mealy bugs. Insects were resistant to the soap and water combination so horticulture oil was applied to the trees. Horticulture oil was applied on overcast days to prevent burning of the leaves. Insect damage was minimal in the second pilot study. A combination of soap and water was sprayed on the trees on May 26, 2008 to kill aphids and spider mites. This eliminated the insect problem. Black willow trees were the most susceptible of the tree species to insect infestation in both pilot studies.

Plant Quality Evaluation

Evaluation of tree health was determined by collecting plant quality data throughout the pilot study. Monthly tree height, caliper, and visual ratings were taken to monitor the overall growth of the tree.

Height

Tree height was measured in cm and m. Tree heights were taken from the soil line to the apical meristem of the tree. Because black willows have more than one main trunk, the longest branch was measured from the soil line along the branch to the apical meristem. All other trees measured had one leader trunk.

Caliper

Caliper diameters were measured in mm. Calipers of each tree were measured at the base of the trunk even with the top of the pot. To ensure that caliper diameter was measured in the same location each month, a yardstick was placed along the top of the pots in the trough. The caliper was then collected evenly with the yardstick.

Visual Rating

An important factor of tree health is leaf color. Depending on the time of year leaves naturally change color. Insects, disease, and poor nutrition can also cause a tree's leaves to discolor. Therefore the overall leaf color of each tree was given a visual rating monthly. The visual rating helped identify signs of nutritional, insect, and disease symptoms. As expected, all visual ratings for the trees declined in the winter months during dormancy. Leaves were rated on a visual scale from 1 to 6:

- 1 representing no green only yellow or brown foliage, or no leaves.
- 3 representing a lime green color or half yellow and brown foliage.
- 6 representing healthy dark green foliage.

Water Evaluation

Monthly or more frequent water samples were taken throughout the first greenhouse pilot study by PSI and LSU. Input and discharge samples, collected by PSI of water treatments 33%COC, 67% COC, and 100% COC were analyzed using EPA method 8260 for cumene and EPA method 8270 for semi-volatile organic compounds by Pace Analytical. The same water samples collected by LSU were analyzed in the LSU Department of Environmental Science lab using a modified EPA method 8270. The LSU Department of Environmental Science lab did not have the equipment available to analyze water samples by EPA method 8260.

Each week the troughs were filled with water treatments to a designated level. At the end of the week the water level was measured and recorded. The remaining trough water was discarded. The troughs were then refilled to the original designated level. In warmer months, some troughs would dry out faster than others. Therefore, visits to the greenhouse increased (bi-weekly) to monitor water levels. If the trough level dropped below 50% by mid-week, the trough was refilled to the designated starting level. However, the remaining water was not discarded, the trough was simply "topped off". When water was added to or discharged from the troughs, the amount was recorded. Anderson and Walton (1995) conducted a study using soybeans to remediate trichloroethylene (TCE) contamination. They found that soybean were successful at accumulating ^{14}C labeled TCE and that the amount of ^{14}C labeled TCE correlated with the amount of water used by the soybeans. Therefore, we found it appropriate to track the water usage of the trees.

PSI's supplied water tracking samples of the 100% COC, 67% COC and 33% COC water treatments from June 2006 through August 21, 2006 indicated cumene concentrations lower than would be expected from the routinely quarterly monitoring samples for these wells. The tracking samples were collected the day the water was pumped from the wells to provide a fresh supply.

The lowered concentrations of cumene may have been the result of pumping of the required supply water from these wells every two weeks, which could have drawn well recharge that was lower in cumene than the recharge that occurs during a quarterly sampling event done with bailers. Also, it is possible, but unlikely, that the variable speed submersible pump used to pump water from these wells resulted in notable stripping of cumene from the pumped water.

In order to control the amount of cumene in the water treatments, Georgia-Pacific decided to add a spike of certified cumene standard to each treatment to bring the cumene concentration into the intended range for each treatment. The spike for the 100% COC water treatment was 0.2mg/L and the spikes for the other two treatments were proportional. The first treatments on September 7, 2006 were unintentionally over spiked with cumene by PSI because of a calculation error. Upon discovery, this supplied water batch was disposed, the associated supply tanks were cleaned, and a correctly spiked supply of water was provided to the troughs by September 19, 2006. Cumene levels remained unstable in the water treatments despite the spike, resulting in cumene concentrations below the intended levels from October 30, 2006 through March 2007.

It is possible that cumene was lost from the spiked fresh supply water through various mechanisms, including volatilization from the vented supply tank, adsorption to supply or mixing tank walls, or adsorption to sediment in the supply tanks. PSI collected three sets of samples to evaluate cumene loss from the supply tank over the typical storage period of two weeks. Samples of the initial concentration of the 100% NS2 + NS8 treatment versus an "aged mix" several days later were collected on October 3 and 12, October 12 and 30, and November 13 and 21, 2006. The results were used to estimate a factor for cumene reduction over time to apply to calculations of COC mass introduced to the troughs. The cumene reduction factor for early October when weather was hotter was 0.0430mg/L per day, but was 0.0125mg/L per day in

November when the weather was cooler. An estimated cumene reduction factor of 0.068mg/L was used for the period of June – October 2006 and a factor of 0.0125mg/L was used for November 2006 – March 2007 to account for the effects of temperature.

An LSU graduate student analyzed input and discharge samples collected in the second pilot study at the LSU Department of Environmental Science lab. The water samples were analyzed using a modified EPA 8270 method. Water samples were collected monthly on all water treatments.

Water Treatments

There were six water treatments tested in the first pilot study. Two of the water treatments were replicated for experimental error, the DI water (control) and 33% NS2+ NS8 water treatments. All water treatments came from monitoring wells NS2, NS6, and NS8. Wells NS2 and NS8 have elevated levels of the COC's, while the NS6 well has elevated levels of salts. The following is a list of the six water treatments used in the first pilot study:

- 100% Deionized (DI) water (replicated twice) = Control
- 33% NS2 +NS8 diluted with 67% DI water (replicated twice) = 33% COC
- 67% NS2 +NS8 diluted with 33% DI water = 67% COC
- 100% NS2 +NS8 (50% of each well) = 100% COC
- 50% NS6 diluted with 50% DI water = 50%NaCl
- 100% NS6 water = 100% NaCl

Studies have shown that trace amounts of COC's can sometimes improve tree growth. The COC's act similar to fertilizer. Zhang and colleagues, (2002) studied the abilities of the Ladder brake fern to accumulate arsenic. When levels of up to 100mg/kg of arsenate were added to the soil, fern biomass was increased by 64-107% (Zhang et al., 2002). However, adding 50mg/kg of arsenic to the soil resulted in the highest fern biomass production, the highest ratio of

shoot to soil arsenic concentrations, and the highest ratio of shoot to root arsenic concentrations (Zhang et al., 2002). Anderson, (2007) studied the hyperaccumulation potential of three ferns, *Thelypteris palustris*, *Asparagus sprengeri*, and *Lolium perenne* on the contaminant arsenic. She found that the marsh fern when exposed to 500ug/L arsenic, displayed the highest accumulation range (1120 to 5770 ng/g) and the highest bioaccumulation factor (4.94). Indicating that trace amounts of contaminants may at times encourage plant growth. These two studies show that a medium concentration of a classified harmful constituent can sometimes act as a stimulant to plant growth. While these studies focus on arsenic, a heavy metal, on non-woody plant materials, fern, we felt the results were significant enough to utilize a low, medium, and high range of contaminated water concentrations to determine if cumene and 4-cumylphenol, at low and medium rates act as stimulants to tree growth. Additionally, the 33% COC and 67% COC water treatments were used to mimic the natural environment. A tree will naturally draw water in from the groundwater zone as well as the vadose zone which is above the groundwater zone and mostly comprises of rainwater. In this case rainwater should not be contaminated with cumene and 4-cumylphenol and therefore during a full scale planting trees would take up a portion of uncontaminated water from the vadose zone and a portion of contaminated water from the groundwater plume.

Each water treatment was connected to five hydroponic troughs, with the exception of the control water and 33% COC water treatments which were both connected to 10 pipes each since they were replicated twice. There were a total of 5 blocks, 40 troughs, totaling 8 troughs per block. The 33% COC water treatment and the control water treatment were doubled in case trees growing in the 100% COC treatment died. The extra treatments were held in reserve for a follow-on study if the 100% COC treatment exhibited severe damage early in the study. This did not occur; therefore the extra treatments remained throughout the study.

The various blends of groundwater and DI (control) water represent conditions that the immature trees would encounter during a full-scale field planting. The root systems of immature trees will not initially penetrate into the groundwater plume. Even after the taproot system reaches the groundwater plume, the tree will continue to draw water from the vadose zone above the groundwater plume. "The vadose zone is the intermediate medium between the atmosphere and groundwater" (Sung, *et al.*, 2002). Most of a tree's roots are within the top 0.914m of soil. These roots are commonly referred to as feeder roots. When adequate water is supplied by rain, trees obtain most of their water from the feeder roots. However, during drier periods, deep rooted trees will obtain their water from much deeper water sources (The American Horticultural Society, 1982). Water in the vadose zone comes from rain and is highly unlikely to be contaminated with the COCs in this study. Mature tree species would also differ in the ratio of water they would draw from the vadose zone and groundwater plume. Therefore, it is appropriate that some study treatments include less than 100% Stratum III groundwater.

Water treatments in the second pilot study included:

- DI water only (control)
- Low water treatment (DI water spiked with 0.5mg/L cumene and 1mg/L 4-cumylphenol)
- High water treatment (DI water spiked with 1mg/L cumene and 4mg/L 4-cumylphenol)

The water treatments in the second pilot study were much higher in chemical concentrations compared to the first study. Chemical concentrations were increased to better track chemical movement into the soil and tissue. Chemical concentrations were not higher than those previously found in plume water. Well water was not used because it contained soil. Because

varying amounts of soil entered into the water treatments in the first study the chemical concentration was not as accurate as in the second pilot study.

Pace Analytical used methods EPA 8260 for cumene and EPA 8270 for 4-cumylphenol and all analyzed metabolites. The following paragraphs describe instrumental analysis procedures used for this research project when samples were analyzed at LSU. These basic procedures are standard to those used in the LSU Environmental Science lab.

All gas chromatography/ mass spectrometry (GC/MS) analyses use an Agilent 5890 GC system configured with a 5% diphenyl/95% dimethyl polysiloxane high resolution capillary column (30m, 0.25mm ID, 0.25µm film) directly interfaced to an Agilent 5972 MS detector system. An Agilent 6890 series Auto Injector was used for sample introduction into the GC/MS system. The injection temperature was set at 250°C and only high temperature, low thermal-bleed septa are used in the GC inlet. The GC is operated in the temperature program mode with an initial column temperature of 40°C for 4min then increased to 280°C at a rate of 6°C/min and held for 3min. Total run time is 47 minutes per sample. The interface to the MS is maintained at 280°C. Ultra High Purity (UHP) Helium was the carry gas for the GC/MS system.

The mass spectrometer (MS) is operated in the Selective Ion Monitoring (SIM) to maximize the detection of several trace target constituents unique to cumene and 4-cumylphenol. The instrument was operated such that the selective ions for each acquisition window were scanned at a rate greater than 1.8scans/sec with a dwell time of 75ms. At the start of each analysis period or every 12h the MS was tuned to Perfluorotributylamine (PFTBA), an internal instrument standard. A continuing calibration standard was analyzed prior to the analysis of the sample extracts. This standard operating procedure ensured quality assurance/ quality control of the instrument conditions prior to sample analysis.

Spectral data was processed by Chemstation™ Software using a customized data analysis method developed by the Department of Environmental Sciences. The analysis method was run on each sample and results in raw integration data that is transferred to an Excel spreadsheet program for quantitative analysis. A macro printout was also generated and contained the extracted ion chromatography data in addition to raw integration data.

Analyte concentrations were calculated based on the internal standard method. An internal standard mixture, composed of naphthalene-d_8, acenaphthene – d_{10}, chrysene-d_{12}, and perylene-d_{12} (at concentrations of 10ng/uL) was spiked into the sample extracts just prior to analysis. The concentration of specific target analytes was determined by a 5-point calibration and internal standard method.

Electrical Conductivity Evaluation

Electrical conductivity (EC) was monitored bi-monthly to determine effects of the high plume water salts (above 2mS) on the ability of trees to survive. The groundwater plume contains NaCl levels above normal drinking water standards. EC data was collected in all 50% and 100% NaCl water treatments where salt build-up in the soil might have become a problem. EC was recorded using a portable EC meter. The EC meter was rinsed between troughs. Because well water from NS6 well was not used in the second pilot study, EC was not measured in the second pilot study.

Soil and Plant Tissue Sampling Methods

Baseline samples including soil as well as tree root and shoot tissue were collected for each tree species to determine whether the COCs were present in the plant species prior to the greenhouse study. Baseline samples were then compared to final soil and root and shoot plant tissue samples collected at the end of the study. The presence of the COCs or their metabolites

found in the final root and shoot tissue samples would indicate the ability of the tree species to phytostabilize the COCs or degrade COCs if metabolites were present.

Soil COC Sampling Methods

Baseline samples of soils were taken prior to the start of the pilot greenhouse study. Five composite samples were taken of the potting medium. Laboratory analyses performed by Pace Analytical lab were conducted to determine if the COCs were present in the soil prior to the first pilot study. Pace Analytical lab used EPA method 8270 to detect the presence of the semi-volatile compounds (SVOCs) including 4-cumylphenol, α, α- DMBA, acetophenone, α-methylstyrene, and phenol were analyzed using EPA method 8270. Pace Analytical lab used EPA method 8260 to detect the presence of cumene a volatile organic compound (VOC) in the soil samples. Other semi volatile organic compounds known as Tentatively Identified Compounds (TICs) were analyzed by EPA method 8270. Georgia-Pacific decided not to analyze soil samples for cumene (first year only) as they emphasized that cumene would not normally be found in soil mixes or native soil.

Concluding the greenhouse study, soil samples were collected by removing most of the loose soil from the pot and plant roots. Once the soil in the selected pot was in a pile, two 0.11L jars were filled with the soil and labeled. Soil was analyzed by Pace Analytical lab in the first pilot study and by LSU in the second pilot study. Pace Analytical used EPA method 8270 to detect the presence of SVOCs present in soil and EPA method 8260 to detect the presence of VOCs present in the soil.

Soil samples were taken to LSU for analysis of cumene and 4-cumylphenol for the second greenhouse study. Final soil samples were collected from pots of each tree species in each water treatment. A total of four samples per tree species per water treatment were analyzed for the COCs. A blind duplicate, matrix spike and matrix spike duplicate were also taken for analysis.

The total number of initial soil samples was four, and the total number of final soil samples was thirty-nine. The LSU Environmental Sciences lab was not able to identify tentatively identified compounds (TICs). Therefore, this data is not reported for the second greenhouse study.

Soil samples were individually weighed and recorded. The samples were placed in 250mL beakers. Anhydrous sodium sulfate was added to the beaker covering the soil sample. The anhydrous sodium sulfate removes water present in the extract since it is a desiccant. Dichloromethane (DCM) was added to the beaker, covering the mixture. A 1mL aliquot of surrogate standard was then added to the beaker. The purpose of adding the surrogate is to account for percent recovery after extraction. The beakers were the placed in a FS14H Fisher Scientific sonicator for ten-minute intervals. After sonication, the DCM was poured out of the beaker through a funnel of anhydrous sodium sulfate into a 250mL rotary evaporation flask. The sample was extracted with DCM three times. The flasks were then placed on a BUCHI R-114 rotary evaporator at 80rpm. A vacuum pump was used to distill the samples to 1mL. The 1mL extraction was then placed in a 2mL GC/MS Agilent crimp top vial. Ten µL of internal standard was added to the vial. The extracted samples were then put on a GC/MS for analysis of cumene and 4-cumylphenol using a modified EPA method 8270. Media samples were analyzed using gas chromatograph/mass spectrometer with a J and W DB5 30m by 0.25mm by 0.25µm column. The temperature program had an injector temperature of 250°C. The detector temperature was set at 280°C. The initial temperature was 40°C and increased to 280°C at a rate of 6°C/min. The final hold time was 280°C for 3 min.

Plant Tissue COC Sampling Methods

In addition to soil samples, two replications from each tree species prior to the start of the greenhouse studies were sent to Pace Analytical lab for analysis of the COCs in the plant tissue. The plant samples were divided into roots and shoots separately. The soil was completed washed

off of the tree's roots with DI water before being sent to Pace Analytical lab. Plant samples were wrapped in foil and put into 2 gallon-sized zip lock bags and placed on ice before shipping to Pace Analytical lab. Pace Analytical lab used alfalfa as the plant matrix material to determine the method detection limit (MDL) of the COCs in the plant root and shoot tissue. For the semi-volatile organic compounds (SVOCs) EPA analytical method 8270 was used. For the volatile organic compound, cumene, EPA analytical method 8260 was used.

Concluding the first greenhouse study, replicates of the tree species were again sent to Pace Analytical lab for analysis of the tree tissue. Not all replicates of tree species were sent to Pace Analytical lab for final sampling of the COCs and TICs. The other replicates were used for nutrition sampling. Table 2 displays the tree replications that were selected for final COC sampling during the first pilot study.

Table 2. Number of Replicates of Trees Selected for Final Sampling of Constituents of Concern

		Water Treatments		
Species	**Control**	**100% COC**	**67% COC**	**33% COC**
Bald cypress	2	4	4	4
Black willow	2	4	4	4
Eastern red cedar	2	4	0	0
Spruce pine	0	0	0	0
Water oak	2	4	0	0

The numbers in table are replicate numbers of each tree species that were sent for COC sampling.

Samples from all three COC well treatments (33%, 67%, and 100% COC) as well as the control were taken for the black willow trees. This was decided because the black willow tree is a widely used tree species in phytoremediation projects and had excellent visual ratings and survival rates in the treatment water. The bald cypress tree species were sampled from all three COC (33%, 67%, 100% COC) well treatments as well as the control. The bald cypress tree has a much longer taproot than the black willow tree species. The bald cypress trees also had excellent

survival rates in all water treatments. Eastern red cedars and water oak trees were only sampled for COCs in the control and 100% COC water treatments because of Georgia-Pacific's budget considerations. The 33% COC and 67% COC water treatments were analyzed for black willow and bald cypress to determine if a small amount of the constituents of concern had any effects on tree species. The spruce pine was not sampled in any of the COC treatments because of its overall poor survival rates. Survival of the tree species is discussed in more detail in the results section.

The 50% and 100% NaCl well water treatments were not analyzed for any of the COCs. The main objectives of subjecting tree species to the 50% and 100% NaCl well water treatments was to determine if the proposed tree species would survive higher than normal NaCl levels normally found in the NS6 well. "Concentrations of chloride in external solutions of more than 20mM can lead to toxicity in sensitive plant species"(Marschner, 1995).

Tree shoots (lower portions of the stem) and roots were sampled for the COCs. The entire root mass was sent to Pace Analytical for analysis. The lower 100g of tree trunk were sent to Pace Analytical. The roots were removed from the trunk by cutting the stem immediately above the first root to protrude off of the trunk. A small portion of the bottom trunk was below the soil line and included in the roots sample. The roots were then washed in DI water. The entire root mass was wrapped in foil, doubled zip lock bagged, and labeled. The bags were put on ice and immediately sent to Pace Analytical. All leaves and branches were removed from the lower portion of the trunk. One hundred grams of trunk tissue was needed for each sample. Therefore, the lower trunk tissue was taken until 100g were reached. Some species had a large portion of woody materials left over after the bottom trunk was weighed. These species included the bald cypress and some water oaks. The eastern red cedars needed more than the main trunk to reach 100g of plant material, so some branches were added to the sent sample. After using the entire

trunk of the tree, branches without needles were then used to supplement the trunk material for analysis. A few of the selected eastern red cedars did not weigh 100g even with the entire trunk and all branches, not the needles. In cases like this, what tissue mass that was available, was sent to Pace Analytical lab for analysis. The bottom portions of the trunks were wrapped in foil, double bagged in zip locks and labeled. The samples were put on ice and sent to Pace Analytical lab. Tree leaves and needles were not analyzed in this study for the constituents of concern because of cumene and 4-cumylphenol's large K_{ow} values, it was decided that it was not reasonable to assume that the COCs would be able to be translocated through the xylem up the tree.

At the end of the second pilot study, four root sample replicates of each tree species in each water treatment were also sent to Pace Analytical lab for analysis of COCs and their metabolites. A total of twelve initial root samples and thirty-six final root samples were sent for analysis. Soil was carefully washed away from the roots using DI water. The roots were then weighed and wrapped in foil. Once wrapped, the roots were labeled and placed into 7.57L sized zip lock bags and placed on ice before being shipped to Pace Analytical. Pace Analytical analyzed the tissue samples using EPA method 8260 for cumene and EPA method 8270 for 4-cumylphenol.

Nutrition Sampling

In addition analyzing soil and plant tissue samples for the presence of COCs, four replications of each tree species were collected and analyzed for nutritional deficiencies. The samples were dried in an oven for seven days and weighed to determine dry weight of tree species prior to the pilot studies. The dry weight plant tissue was divided into root and shoots. Dry weights were collected by LSU.

In the second greenhouse study, 4 trees of each species in each water treatment were selected for final nutrition sampling. Roots were divided from tops and analyzed separately. Roots were washed with DI water to remove soil. Roots and tops were dried in an oven. The samples were ground and sent to the AG Chemistry lab for nutritional analysis using ICP Group 1. The final low and high water treatment concentrations of elements were compared to the DI water treatment concentrations of elements for each tree species.

Spruce pine trees were not analyzed for COCs in the final sampling because they had low survival rates in the treatment water. However, four spruce pine replications in each water treatment, including the 100% NaCl water treatment were sampled to determine if a nutrient deficiency, instead of a response to COCs was responsible for the lack of survival. Spruce pine replicates were dried in a VWR Scientific Inc. VWR 1660 model dryer at 65°C, weighed, ground using a 3/4HP Wiley Mill from Pennsylvania, USA then sent to LSU's Agriculture Chemistry lab for nutritional analysis. Furthermore, 4 replications of bald cypress, eastern red cedar, black willow, and water oak in the 50% NaCl water treatment and 100% NaCl water treatment were analyzed for nutrients as well. All trees species in the salt-water treatments were sampled because the salt-water treatments were not sent to Pace Analytical for COC analysis. The major objective of the 50% and 100% NaCl water treatments was to determine if the species would be able to survive contact with the high levels of salinity. Nutritional data from all five tree species in these two water treatments would better define if salt or nutrient deficiencies were the cause of low visual ratings and or growth stunting. Table 3 represents the number of replications taken from each tree species in the particular water treatment.

The roots and tops of each tree replication were analyzed separately. 11 analytes were sampled for. The 11 analytes were Boron (B), Calcium (Ca), Copper (Cu), Iron (Fe), Magnesium (Mg), Manganese (Mn), Phosphorus (P), Potassium (K), Sodium (Na), Sulfur (S), and Zinc (Zn).

The concentrations of each analyte are reported in ng/mL in the results section. Nutrient samples were statistically analyzed using Agriculture Chemistry ICP Group 1.

Table 3. Number of Replicates Analyzed for Nutrient Samples of Trees

	Water Treatments					
Tree Species	**DI**	**33% COC**	**67% COC**	**100% COC**	**50% NaCl**	**100% NaCl**
Bald cypress	0	0	0	0	4	4
Black willow	0	0	0	0	4	4
Eastern red cedar	0	0	0	0	4	4
Spruce pine	4	4	4	4	4	4
Water oak	0	0	0	0	4	4

The numbers in table represent that number of replicates of each tree species that was analyzed for nutrient concentration in tree tissue.

Prior to the start of the second pilot study, four replicates of each tree species (24 total samples) divided into roots and tops were sent to the LSU Agriculture Chemistry lab for analysis of basic nutrients. After the study was complete, four replicates of each tree species divided by roots and tops from each tree species and each water treatment were sent to the LSU Agriculture Chemistry lab for analysis of basic nutrients. A total of 72 final samples were submitted for analysis during the second pilot study. The analysis used was a basic ICP group 1.The analytes were P, K, Ca, Mg, Na, Fe, Zn, Mn, S, Cu, and B. The purpose of testing the tree tissue for nutrition was to determine if growth differences in tree height, caliper, and visual ratings were a result of chemicals present in the water or nutrient deficiencies.

Sludge COC Sampling Methods

After the final soil and tissue samples had been taken, samples of sludge material at the bottom of troughs were collected. Sludge is a combination of sediments from treatment water, soil from pots, and decaying roots. All sludge from each trough was put into plastic vials and brought to LSU's toxicology lab for analysis. These samples were run to determine if cumene or 4-cumylphenol had attached to the sediments that settled out of the treatment water.

The sludge extraction procedure is as follows. First the weight of each sample was measured in grams. The sample was put into a 200mL beaker and anhydrous sodium sulfate was added to further remove any moisture in the sample. Dichloromethane (DCM) was then poured into the 200mL beaker, over the sample and an anhydrous sodium sulfate mixture. One mL (1000µl) of surrogate standard was then added to the mixture, carefully making sure that the tip of the needle was under the DCM. The purpose of the surrogate standard is to later validate the efficiency of the extraction. The beaker containing the sample was then placed in a FS14H Fisher Scientific sonic dismembrator for ten minutes. While the sample was on the sonic dismembrator, 2 Whatman 15.0 cm No. 40 ashless filter papers were folded in half and placed in a glass funnel to act as a filter. The funnel was placed on a rotary evaporator flask. Anhydrous sodium sulfate was placed inside the filter paper lined funnel. DCM was added to moisten the anhydrous sodium sulfate in the funnel. The DCM from the sample in the 200mL beaker was then poured into the funnel over the rotary evaporation flask. This was carefully completed so that the actual sludge sample did not get into the funnel, only the DCM. Additional DCM was then added to the funnel and added to the beaker containing the sludge sample and placed on the sonic dismembrator for an additional 10mins. Once again the DCM from the sample was poured into the funnel. This process was repeated 3 times. Next, the cool and hot water baths were used. When the cool water bath temperature was below 15˚C, it was ready for use. The funnel was removed from the rotary evaporation flask. The flask was positioned so that the bottom portion of the flask was in the water, but the flask itself did not touch the side of the hot water bath. The rotary evaporator was turned on so that the flask began to turn then the vacuum pump was turned on. Before any samples were placed on the BUCHI R-114 rotary evaporator, a blank sample of DCM was run dry. All samples were reduced to a final volume of 1mL. If more than 1mL was left in the sample, it was denitrified to reduce the final volume to 1mL. If the sample was run too long, and

less than 1mL of sample was left, DCM was added to the sample to a final volume of 1mL. The final volumes were pipette into 15mL tubes. Kimwipes and DCM were used to clean the portion of the rotary evaporator that went into each flask between samples. The purpose of the rotary evaporator was to condense the samples. It uses a distillation process to take the DCM out of the sample and leave behind a concentrated sample including the COC's, in this case, cumene and 4-cumylphenol. The 1mL sample was then placed into a 2mL Gas chromatograph mass spectrometer (GC/MS) Agilent crimp top amber vial along with 10mL of internal standard and capped. Samples were then run on the GC/MS.

A total of 24 sludge samples were collected in the second pilot study. The sludge samples consisted mostly of water; therefore, the sludge extraction method used in the first study was not used for the second study. Instead, liquid to liquid extractions were completed to analyze the sludge in the second greenhouse study.

In year two, sludge samples were poured into graduated cylinders and the volumes were recorded. Samples were then carefully poured into separation flasks that were held on ring stands directly above a 250mL rotary evaporator flask with a funnel filled with anhydrous sodium sulfate. DCM was added to the separation flask. A 1mL aliquot of surrogate standard was added to each separation flask. Each separation flask was shaken three times, each time allowing the air out of the flask to reduce pressure. After agitation, the separation flask was placed back onto the ring stand so that the sample would settle. The DCM in the sampled was drained onto the funnel holding the sodium sulfate then into the rotary evaporator flask. This procedure was completed three times for each sample. Samples were then placed on the rotary evaporator and distilled to a 1mL aliquot. The extracted samples were then placed into 2mL Agilent crimp top vials with 10ul of internal standard and placed on the GC/MS for analysis. Sludge samples were analyzed using the same method that was used for the soil samples.

Methods Changed for the Second Pilot Study

Several changes took place in the second pilot study. Most of the changes occurred because of results from the first pilot study. Some changes occurred so that a more accurate measure was used to determine an optimum tree species. The main changes that occurred included:

- Water usage study by species
- Study included three tree species (bald cypress, black willow, and cottonwood)
- Three water treatments used
- All water and soil samples analyzed at LSU
- Only root tissue was analyzed

CHAPTER 4

FIRST PILOT STUDY RESULTS (2006-2007)

RESULTS- FIRST GREENHOUSE PILOT STUDY

Environmental Conditions

Temperature

A high/low thermometer and a data logger (Hobo) were used to record the average greenhouse temperatures. Throughout the study, the greenhouse temperature and relative humidity were recorded every 15mins. Monthly temperature means are shown in Figure 3.

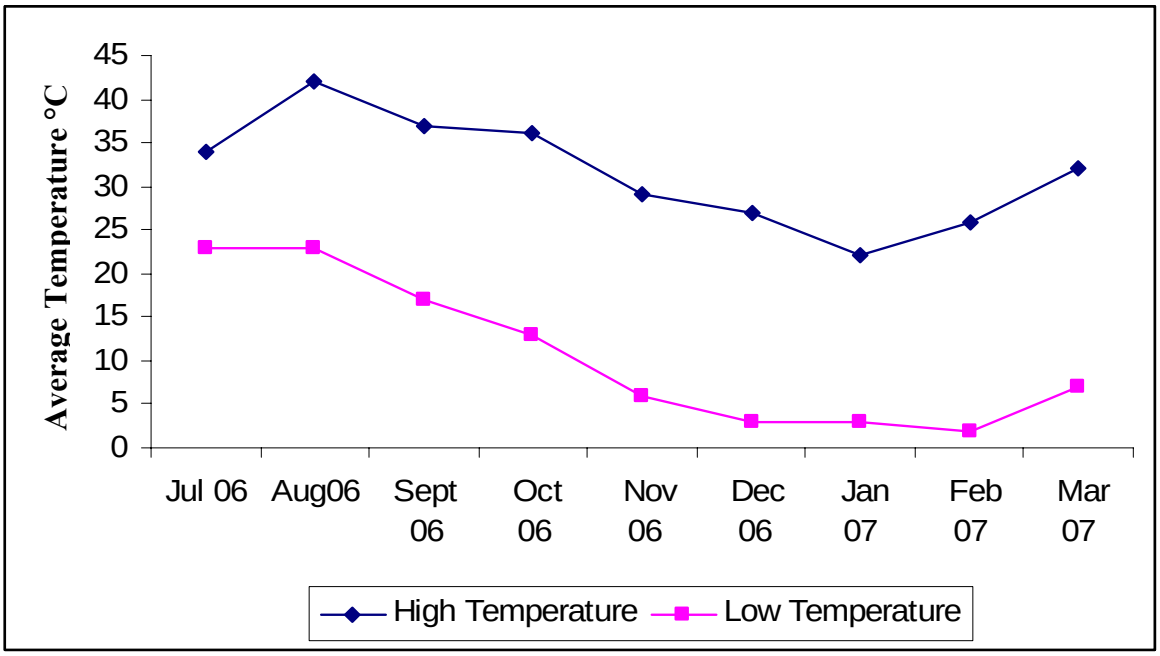

Figure 3. Year 1 Mean Greenhouse Temperature ˚C

Temperature has an effect on growth. Generally trees stop growing in temperatures over 38˚C. July, August, September and October were on average the warmest months in the greenhouse. The coolest month was February.

Relative Humidity

Because the data loggers were purchased after the study began, the relative humidity and temperature recordings from the data loggers began on July 19, 2006 and ended on March 31, 2007. Data was missing from January 30, 2007 to March 15, 2007 because of low battery levels

in the data loggers, therefore, relative humidity data was collected from the local weather station. Figure 4 shows the relative humidity in the greenhouse.

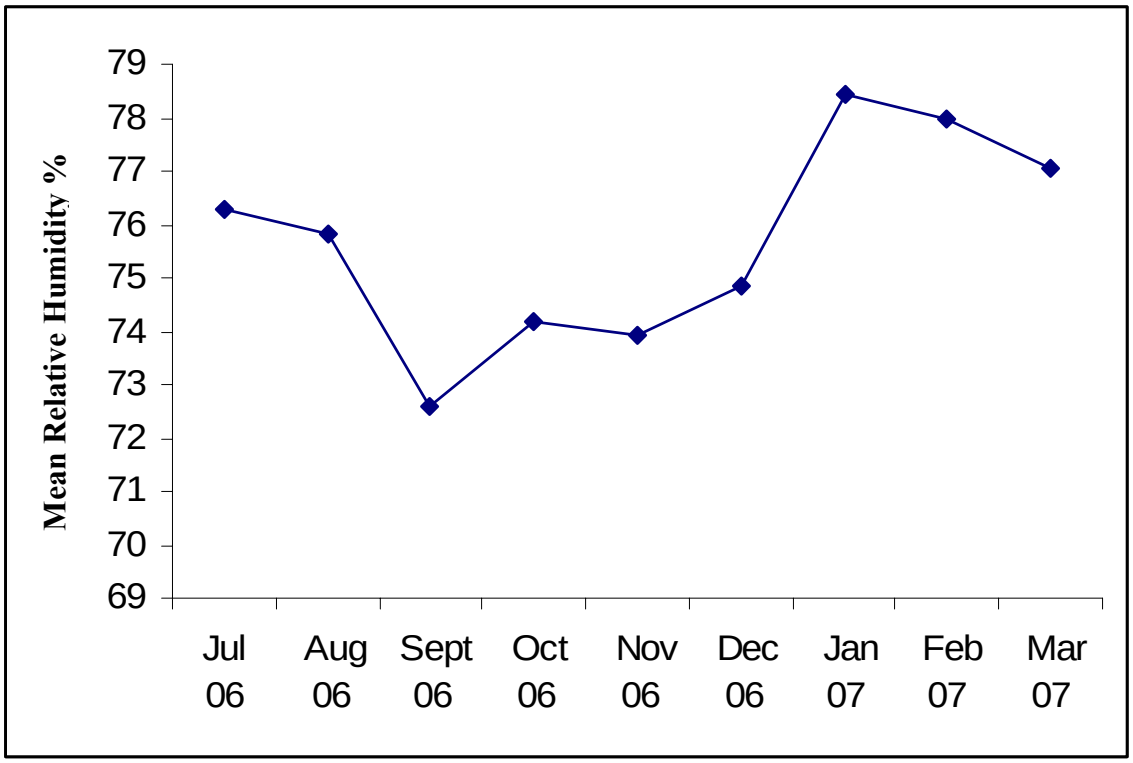

Figure 4. Year 1 Mean Greenhouse Relative Humidity Percentage

The relative humidity in the greenhouse remained relatively constant throughout the study, ranging from 72.5 to 78.5%. Plants tend to transpire less on days with high relative humidity and cooler temperatures.

While relative humidity remained relatively stable in the greenhouse, the temperature fluctuated between 12 and 30°C. In general, most plants stop growing around 100°F or about 38°C. Respiration rises while synthesis of sugars through the process of photosynthesis slows at temperatures at and above 38°C. Therefore, monitoring the greenhouse temperature was important in this study in order to determine differing variables that might have caused a decline in plant quality. Greenhouse temperatures above or below the optimum growing range could

have detrimental effects on plant quality. However, the greenhouse temperatures remained in a range that did not impede plant growth.

Water Monitoring

There were six water treatments tested in the first pilot study. They included; Deionized water (control); 33% COC water; 67% COC water; 100% COC water; 50% NaCl water; and 100% NaCl water. The volume of water that was added and discharged from the individual troughs was monitored throughout the study. Table 4 provides the calculated average amount of water that was used by plants in each block. There was one trough per block for all water treatments with the exception of the 33% COC and control water treatments. These water treatments had two troughs per block. This was intentionally done to ramp up water treatments if trees died immediately upon contact with full strength well water. The extra treatments were not needed.

Monitoring the amounts of input and discharge water from troughs was important because it enabled calculation of the amounts of cumene and 4-cumylphenol that that trees were exposed to. The mass of other COC's in the water provided to the troughs was negligible.

Table 4. Mean Mass of Cumene and 4-Cumylphenol Added to the Treatment Water

Water Treatment	Volume of Water (Gallons)	Volume of Water (Liters)	4-Cumylphenol Mass (mg)	Cumene Mass (mg)
100 % COC	98.01	374.02	236.38	99.98
67% COC	98.79	373.97	84.11	76.88
33% COC	97.35	368.51	35.68	37.13

The values in the table reflect the average water used in each block over the course of the study. These values do not reflect the water that was discharged from troughs.

Approximately the same amount of water was taken up by each of the 5 replicate blocks in each of the three COC treatments. As previously discussed, the concentrations of cumene and 4-cumylphenol were variable in the water pumped from wells NS2 and NS8 over the length of the study.

The total mass of cumene added to the troughs for the 100%, 67% and 33% COC treatments was roughly equivalent to the intended proportions. The average concentration of cumene for the 100% COC treatment for the whole period (total mass of COC divided by total liters of water) was 0.267mg/L, which is somewhat lower than intended but similar to conditions that were currently observed during quarterly monitoring events documented by Georgia-Pacific (May 2007 cumene values: NS2 = 0.0682 mg/L, NS8 = 0.103 mg/L, average = 0.086 mg/L).

The total mass of 4-cumylphenol added to the troughs for the 100%, 67% and 33% COC treatments was not equivalent to the intended proportions, with the 67% and 33% COC treatments having less total mass than intended. The average concentration of 4-cumylphenol for the 100% COC treatment for the whole period (total mass of COC divided by total liters of water) was 0.632mg/L, which is somewhat lower than intended but similar to conditions that were currently observed during quarterly monitoring events documented by Georgia-Pacific (May 2007 4-cumylphenol values: NS2 = 0.111mg/L, NS8 = 1.47mg/L, average = 0.790mg/L).

Plant Quality

Initial Versus Final Quality Indicators

Once a month, caliper, height, and visual rating measurements were collected for each tree. The average caliper in mm, height in cm and visual rating for each species by treatment during the beginning of the study June 2006 and the end of the study March 2007 is shown in a Table AC.1 in the Appendix.

Caliper

Growth differences between the first and last month aid in determining the effects of the treatment water on tree growth. Table 5 presents the statistical differences in caliper measurements of each species by treatment during June 2006 and March 2007.

Table 5. Statistical Analysis of June 2006 and March 2007 Caliper Measurements

	Caliper (mm)				
	Species				
	Bald cypress	**Black willow**	**Eastern red cedar**	**Spruce pine**	**Water oak**
100% NaCl Well Water					
June	11.4[Z]	8.5	10.2	3.9	5.6
March	19.6	9.9	13.5	5.8	10.2
Significance	*	NS	NS	*	*
50% NaCl Well Water					
June	12.9[Z]	10.1	11.8	4.1	6.5
March	20.1	10.5	15.9	5.4	11.4
Significance	*	NS	*	NS	*
100% COC Well Water					
June	10.7[Z]	10.4	9.5	4.3	6.4
March	19.3	11.9	13.9	5.6	12.5
Significance	*	NS	*	NS	*
67% COC Well Water					
June	13.3 [Z]	9.2	11.2	5.7	7.3
March	22.8	12.1	14.6	7.3	11.8
Significance	*	*	*	NS	*
33% COC					
June	11.9 [Z]	9.6	12	4.6	5.3
March	18.9	11.8	15.7	6.2	11.8
Significance	*	*	*	NS	*
DI Water (Control)					
June	9.8 [Z]	9.8	11.8	5.2	7.2
March	24.4	13.3	14.7	6.9	12.4
Significance	*	*	*	NS	*

[Z] Means within column blocks were statistically compared using Duncan's PROC GLM. N=10. NS= not significant; * $p \leq 0.05$.

Water from the 100% NaCl (NS6) monitoring well read high in salinity measurements. Trees that were subjected to 100% NaCl water was used to determine salt tolerance of each species. The caliper measurements of black willow and eastern red cedar trees exposed to treatment did not significantly increase during the study. However, caliper measurements of the bald cypress and water oak trees did significantly increase ($p \leq 0.005$). The significant increase in caliper measurements for the bald cypress and water oak tree species indicates salinity tolerance in these two species.

Based on these results bald cypress and water oaks are considered for full scale planting over the plume. Caliper measurements of the spruce pine trees also significantly increased ($p \leq 0.05$) throughout the study but were such poor quality trees that they are not considered for full scale phytoremediation.

The second treatment (50% NaCl) was a blend of 50% NS6 well water and 50% DI water. The NS6 well water was diluted to mimic periods of high precipitation. During periods of high precipitation, trees obtain most of the water they need from the vadose zone. The vadose zone is immediately above the ground water zone and typically consists of rainwater. Normally rainwater should not be contaminated with COC's or with high salinity levels. It is unlikely that the contaminated groundwater plume would move upward. The Stratum III sediment level consists of two layers of clay with a clay/silt layer between. It is more likely that water will move horizontally in this Stratum. Caliper measurements of bald cypress ($p \leq 0.0005$), eastern red cedar ($p \leq 0.005$) and water oak's ($p \leq 0.0005$), growing in 50% NaCl water, significantly increased throughout the study. These results indicate that during periods of high precipitation, these species would tolerate and significantly increase in growth when subjected to a blend of the NaCl water and rainwater.

The third treatment was a blend of 50% NS2 and 50% NS8 well water (100% COC water). Typical analytical recordings of cumene and 4-cumylphenol have been high in these wells. Therefore, this treatment was considered the full strength contaminated plume water treatment. Bald cypress ($p \leq 0.05$), eastern red cedars ($p \leq 0.05$), and water oaks ($p \leq 0.005$), growing in the 100% COC water had significantly larger caliper measurements by the end of the study. Black willow caliper measurements increased but not significantly.

The fourth treatment was a dilution of 100% COC water. It consisted of a blend of 67% water from well NS2 and NS8, 33% from each, and was diluted with 33% DI water (67% COC

water). This medium strength contaminated water treatment was used to mimic tree uptake of water during high precipitation and or tree growth prior to the taproot fully entering the plume. Sixty-seven percent COC water is a treatment that mimics a real world environment where the tree translocates water from the groundwater zone but also translocates water from the vadose zone. Caliper measurements of all tree species growing in 67% COC water, except the spruce pines, significantly increased by the end of the study. Bald cypress, black willow, eastern red cedar, and water oak significantly increased by ($p \leq 0.0005$) ($p \leq 0.05$) ($p \leq 0.005$) ($p \leq 0.005$) respectively.

The fifth treatment, which was replicated twice, was a blend of water from wells NS2, NS8 and DI water. Water in this treatment included 16.5%water from each NS2 and NS8 and 67% DI water (33% COC water). This was the lowest treatment of contaminated water that trees were subjected to. All tree species with the exception of spruce pine significantly increased in caliper measurements when subjected to the 33% COC water treatment.

The use of DI water alone served as our control water treatment. The control treatment like the 33% COC treatment was replicated twice in each block. The trees growing in DI water were not affected by the COCs. Variables potentially affecting the DI trees were high heat, insect damage, sun direction, etc. All species significantly increased in caliper diameter in the DI water, with the exception of the spruce pine.

Spruce pine did not increase in caliper in the control water, therefore it cannot be concluded that the constituents of concern were associated with the lack of growth in this species. The overall starting quality of the spruce pines was low.

Statistical analysis was conducted on the mean caliper measurements taken in March 2007 comparing the control trees to the trees growing in each water treatment. Table 6 displays

the significant results for the mean tree caliper measurements between treatment and control trees.

The only statistical differences in control and treatment final tree caliper measurements were found in the 100% NaCl water treatment. This treatment was considered the full strength salinity treatment. The black willows and water oaks growing in the 100% NaCl water treatment had significantly smaller caliper measurements than the control trees growing in DI water. This suggests that the salinity in the closed and capped impoundment area plume water has an effect on the growth of these two species.

Height

In addition to caliper measurements, height measurements were recorded monthly. Table 7 represents the statistical changes in height between the months of June 2006 and March 2007.

Bald cypress ($p \leq 0.005$) and spruce pine trees ($p \leq 0.005$) subjected to the 100% NaCl water significantly increased in height. Bald cypress mean caliper measurements also significantly increased from June to March, indicating that this tree is not impacted by the salinity levels in the closed and capped impoundment groundwater plume. The other tree species did not have significant increases in height when exposed to the 100% NaCl water.

Bald cypress in the 50% NaCl water significantly increased ($p \leq 0.005$) in height. The black willow tree significantly increased ($p \leq 0.05$) in height as well. The bald cypress and black willow trees had significant increases in their mean heights at the end of the study, when subjected to the 100% COC water treatment. Although not significant, there was a height increase in the other tree species; the spruce pine's growth being very low.

All tree species with the exception of the spruce pine significantly increased in height when subjected to the 67% COC water treatment. These results indicate that all tree species with

the exception of spruce pine are possible candidates for full scale planting and phytoremediation of the closed and capped impoundment plume.

Table 6. Statistical Results of Final Mean Calipers of Control and Treatment Trees

Species	DI (mm)	Water Treatment (mm)	Significance
		100% NaCl water	
Bald cypress	22.44	19.60	NS
Black willow	13.32	9.90	*
Eastern red cedar	14.69	13.46	NS
Spruce pine	6.89	5.80	NS
Water oak	12.43	10.16	*
		50% NaCl water	
Bald cypress	21.82	20.10	NS
Black willow	13.32	10.50	NS
Eastern red cedar	14.69	15.90	NS
Spruce pine	6.89	5.40	NS
Water oak	12.43	11.42	NS
		100% COC water	
Bald cypress	22.44	19.34	NS
Black willow	13.32	11.96	NS
Eastern red cedar	14.69	13.86	NS
Spruce pine	6.89	5.62	NS
Water oak	12.43	12.48	NS
		67% COC water	
Bald cypress	22.44	22.76	NS
Black willow	13.32	12.06	NS
Eastern red cedar	14.69	14.58	NS
Spruce pine	6.89	7.32	NS
Water oak	12.43	11.78	NS
		33% COC water	
Bald cypress	22.44	18.87	NS
Black willow	13.32	11.83	NS
Eastern red cedar	14.69	15.73	NS
Spruce pine	6.89	6.19	NS
Water oak	12.43	11.78	NS

Means within rows are significantly different at * $p<0.05$; NS is not significant. N= 10 for the control means. N= 5 for the treatment means for all water treatments accept the 33% COC water treatment where N=10 for both treatment and control trees.

All tree species with the exception of the black willow gained significant height throughout the study. This indicates that the tree species can withstand contact with diluted Stratum III groundwater.

Table 7. Statistical Analysis of June 2006 and March 2007 Height Measurements

	Height (cm)				
	Species				
Water Trt and Sample Period	**Bald cypress**	**Black willow**	**Eastern red cedar**	**Spruce pine**	**Water Oak**
100% NaCl Water					
June	95.5 [Z]	82.4	65.4	28.6	47.1
March	126.8	85.4	94.7	40.6	63.0
Significance	*	NS	NS	*	NS
50% NaCl Water					
June	100.5 [Z]	63.1	65.9	29.5	51.6
March	135.1	89.0	87.4	39.0	89.0
Significance	*	*	NS	NS	NS
100% COC Water					
June	94.7 [Z]	81.7	65.9	37.3	64.6
March	128.1	111.2	79.8	36.2	79.0
Significance	*	*	NS	NS	NS
67% COC Water					
June	99.4 [Z]	75.1	64.9	38.4	52.8
March	131.0	97.0	93.0	51.6	85.2
Significance	*	*	*	NS	*
33% COC Water					
June	100.8 [Z]	77.6	61.3	33.6	50.6
March	121.3	85.3	84.6	46.5	89.0
Significance	*	NS	*	*	*
DI Water					
June	92.6 [Z]	83.9	64.7	34.2	53.2
March	121.7	101.7	86.6	49.7	102.2
Significance	*	*	*	*	*

[Z] Means within columns were statistically compared using a Duncan's PROC GLM. N=10. NS= not significant; * p≤0.05.

All species had significant increases in height when subjected to the DI water treatment. This is important because it shows that the greenhouse conditions were ideal for tree growth and that these trees also grew significantly when placed in the same environmental conditions as trees growing in contaminated water.

Cumene and 4-cumylphenol are not the only potential problems that the trees will face when planted full scale over and around the groundwater plume. High salts are also a factor. The NS6 well continuously shows high levels of salt, with electrical conductivity (EC) averaging 2.12mS over the period of the study. Therefore, the EC was measured monthly in 100% and 50%

NS6 treatment troughs. The 100% NaCl water had an average EC measurement of 2.09mS, while the 50% NS6 treatment troughs averaged 1.14mS. Because there was never a major build up of salts throughout the study, a leachate test on potting media was not performed.

Statistical analysis was conducted on the mean height measurements taken in March 2007 comparing the control trees to the trees growing in each water treatment. Table 8 gives the results of the differences in height between control and treatment trees for each water treatment.

Table 8. Statistical Results of Final Mean Height's of Control and Treatment Trees

Species	DI (cm)	Water Treatment (cm)	Significance
	Control	**100% NaCl water**	
Bald cypress	121.7	126.8	NS
Black willow	101.7	85.4	NS
Eastern red cedar	86.6	94.7	NS
Spruce pine	49.7	40.6	NS
Water oak	102.2	63.0	*
		50% NaCl water	
Bald cypress	121.7	135.1	NS
Black willow	101.7	89.0	NS
Eastern red cedar	86.6	87.4	NS
Spruce pine	49.7	39.0	NS
Water oak	102.2	89.0	NS
		100% COC water	
Bald cypress	121.7	128.1	NS
Black willow	101.7	111.2	NS
Eastern red cedar	86.6	79.8	NS
Spruce pine	49.7	36.2	NS
Water oak	102.2	79.0	NS
		67% COC water	
Bald cypress	121.7	131.0	NS
Black willow	101.7	97.0	NS
Eastern red cedar	86.6	93.0	NS
Spruce pine	49.7	51.6	NS
Water oak	102.2	85.2	NS
		33% COC water	
Bald cypress	121.7	121.3	NS
Black willow	101.7	85.3	NS
Eastern red cedar	86.6	84.6	NS
Spruce pine	49.7	46.5	NS
Water oak	102.2	89.0	NS

Means within rows are significantly different at NS is not significant; * $p<0.05$. N= 10 for the control means. N= 5 for the treatment means for all water treatments accept the 33% COC water treatment where N=10 for both treatment and control trees.

Water oaks were significantly shorter in the 100% NaCl well water treatment, which served as the full strength salinity treatment. Results indicate that water oaks are not as tolerant as other tested tree species to the salinity in the full strength closed and capped impoundment plume water. There were no significant differences in the heights of any tree species in any of the treatment waters with the one exception of water oak in the full salinity treatment. Visual ratings reported in Figure 7 report the monthly means for eastern red cedars. At the end of the study the visual mean for 100% NaCl treatment eastern red cedar trees was 2.5, which indicated that salinity may have been beginning to affect tree growth, as these trees were almost all yellow or brown. So while the height and caliper measurements of the eastern red cedars were not significantly effected by the presence of the NaCl well water treatment, the visual rating indicated that the tree's health were beginning to decline.

Visual Rating

An important factor of tree health is leaf color. Leaves were rated on a visual scale from 1 to 6: Number 1 represents no green only yellow or brown foliage or no leaves at all. Number 3 represents a lime green color or half yellow and brown foliage. Number 6 represents healthy dark green foliage.

Figures 5 through 9 represent the mean monthly visual ratings by tree species. All bald cypress trees, including those growing in the control water treatment (DI water) have low scores on the visual ratings in the months of December, January, and February. These low visual ratings were given because the bald cypress had shed their leaves. This is a natural process for deciduous trees in winter months. The trees did not die during these months, but went dormant.

Like the bald cypress trees, black willows growing in all water treatments lost leaves during the winter months resulting in low visual rating scores. The trees did not die during these months, but went dormant. The black willows also had lower visual rating scores in September

because of an infestation of aphids and spider mites, which caused severe leaf damage. However, the trees did produce a new crop of leaves. Visual ratings in March remained low for the black willows because they had not fully leaved out before final sampling.

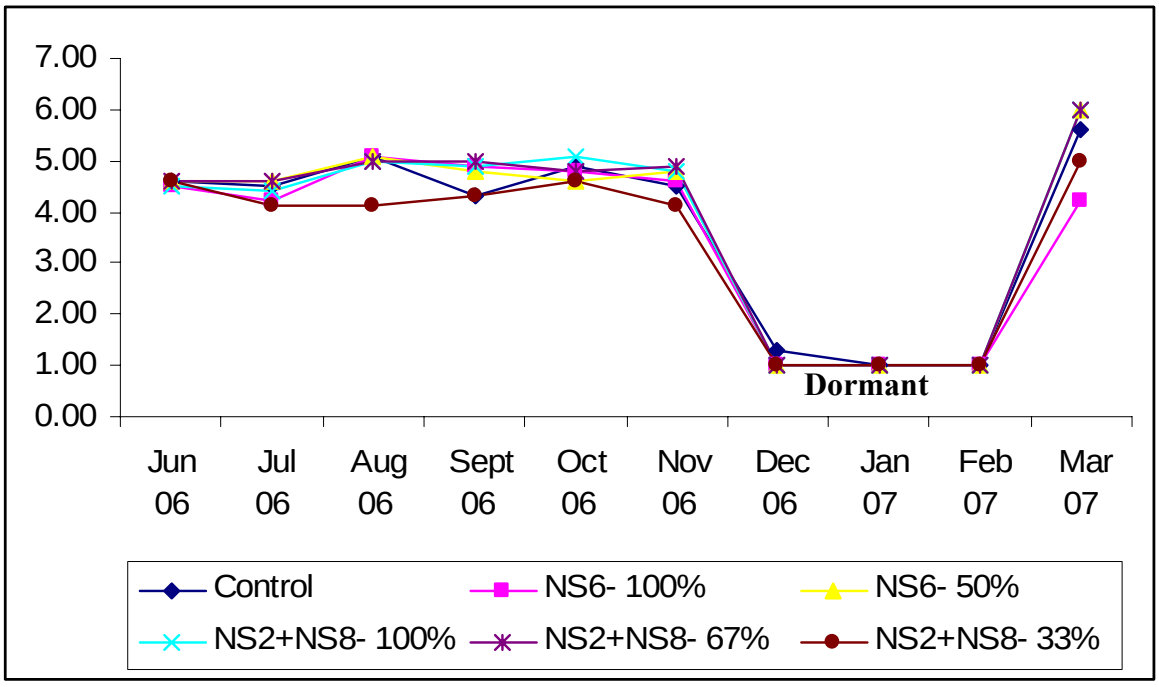

Figure 5. Mean Visual Rating of Bald Cypress Trees

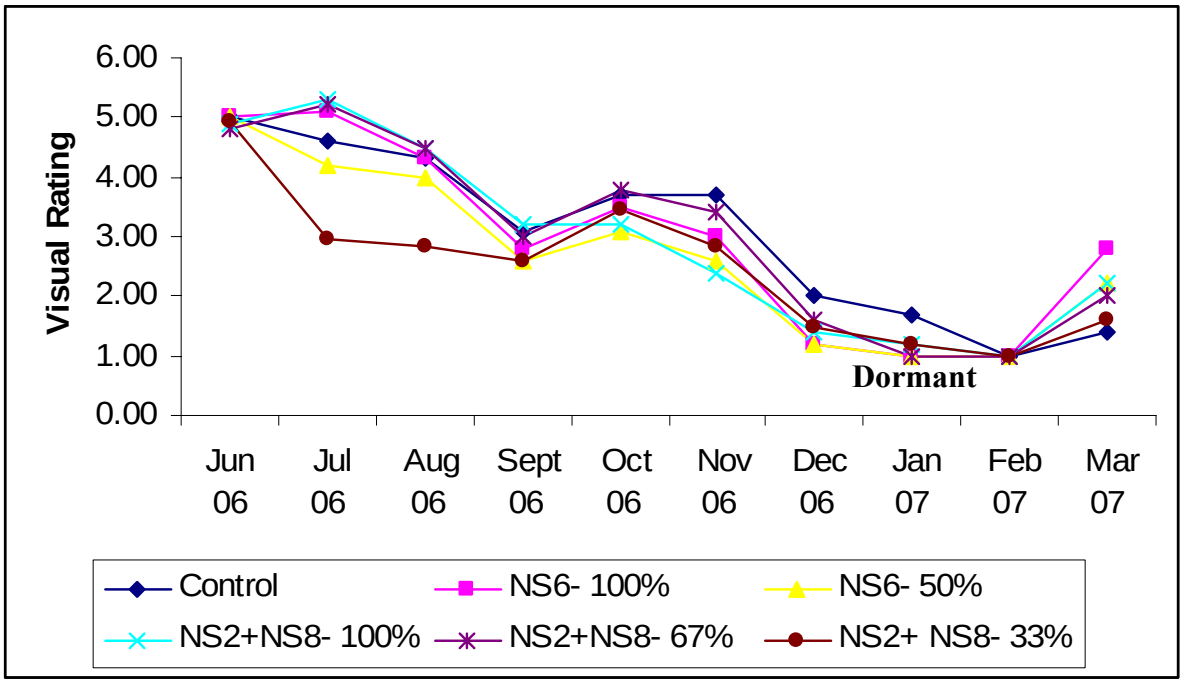

Figure 6. Mean Visual Rating of Black Willow Trees

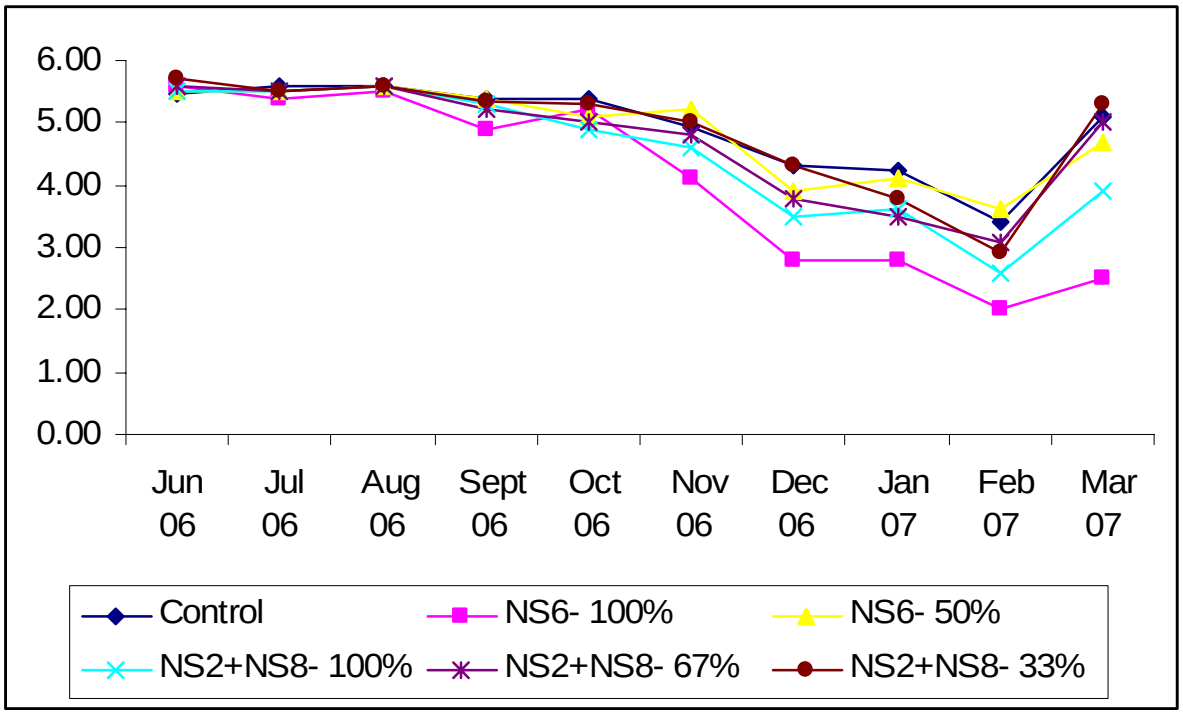

Figure 7. Mean Visual Rating of Eastern Red Cedar Trees

The eastern red cedar trees had lower scores in November, December, and January because they naturally turn purple. This is because the breaking down of the chlorophyll pigments in the winter and showing the dominant anthocynin pigment a purplish color. This is a natural event for these evergreen trees. However, the 100% NaCl or salinity treatment remained low in visual rating throughout the rest of the study. These trees were severely impacted by the salinity in the treatment water, which was a conflicting result as the eastern red cedar is commonly listed as a salt tolerant tree species. If the study had continued for several additional months, it is hypothesized that a decline in growth may have been reported. The 100% COC water treatment trees also exhibited reduced visual ratings in February and March at the end of the study compared to the control treatment.

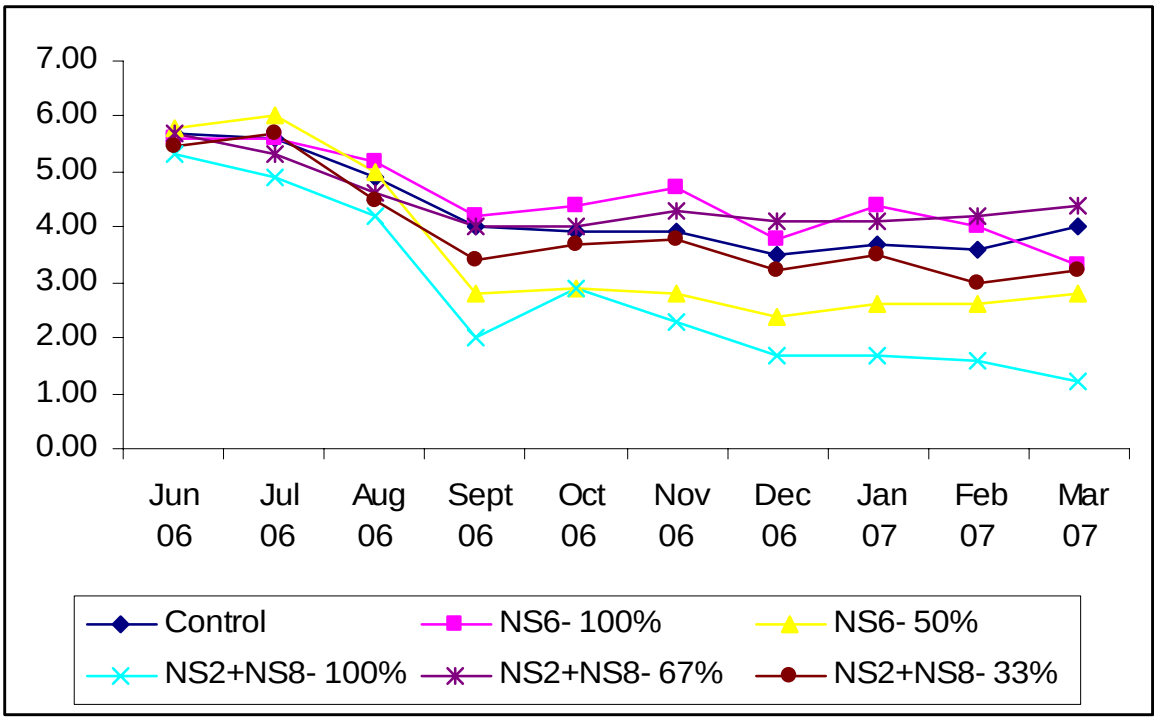

Figure 8. Mean Visual Rating of Spruce Pine Trees

The spruce pine tree species all began the study with dark green needles, thus received high visual rating scores. However, the nursery stock that was used was very poor resulting in low visual ratings throughout the study for this tree species. Spruce pines are an evergreen tree species. They do lose some needles in the winter months. The low visual ratings in the winter were a result of poor nursery stock. All of the spruce pine treatments including the controls exhibited mortality of at least 20 to 30 percent of the specimens (control was 30%), with the 50% and 100% NaCl water treatments and the 100% COC water treatment exhibiting the worst plant health conditions by the end of the study.

The water oaks also had low visual rating scores in the winter months. The scores were not as low as the bald cypress and water oaks because they did not completely defoliate but did lose the majority of leaves. The scores were still low in February and March because the Water oaks had not fully leafed out before final sampling took place.

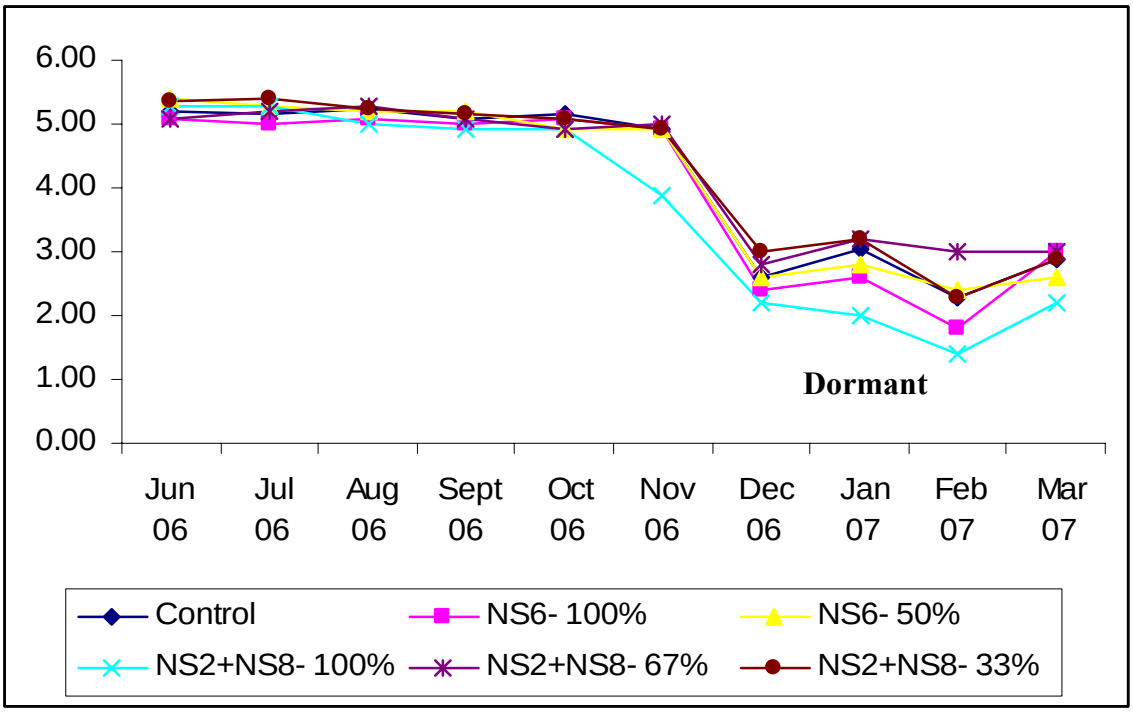

Figure 9. Mean Visual Rating of Water Oak Trees

Plant Tissue Final Sampling

Initial Tissue Samples

Cumene and 4-cumylphenol were not detected in the initial plant tissue samples. The tentatively identified compounds that were detected in the initial plant tissue are shown in the Appendix.

Final Tissue Samples

Cumene and 4-cumylphenol were found in notable concentrations on one plant tissue sample. A black willow tree growing in Block II in the 100% COC water treatment had a cumene concentration of 0.0054mg/kg and 4-cumylphenol concentration of 0.130mg/kg on the roots. Data is displayed in the Appendix in Table AB.1. This is a relatively small amount of parent compound found, considering the cumulative mass of cumene and 4-cumylphenol introduced to the trees throughout the pilot study.

Results for the final tissue sampling in March/April 2007 are provided in the Appendix in Table AB.1. The scope and logic of the sampling were discussed previously under the section entitled Materials and Methods, Sampling. No COCs were detected in the roots and "tops" (also referred to as "shoots") of bald cypress, eastern red cedar and water oak. Spruce pine specimens were not sampled for analysis of COCs as discussed previously.

Certain COCs were detected in black willow tissue. Cumene was detected in the roots of only one black willow specimen for the 100% COC water treatment at a concentration of 0.0054mg/kg, which represents approximately 0.01 percent of the cumene mass that was introduced to this specific trough. Four-cumylphenol was detected in the roots of only two black willow specimens for the 100% COC water treatment at concentrations of 0.130mg/kg and 0.086mg/kg, which represents approximately 0.2 percent and 0.08 percent of the 4-cumylphenol mass that was introduced to these specific troughs. Four-cumylphenol was detected on the roots of one black willow specimen for the 67% COC water treatment at a concentration of 0.093mg/kg, which represents approximately 0.25 percent of the 4-cumylphenol mass that was introduced to this specific trough. Phenol was detected in roots and tops of both control specimens and most of the specimens for the 100%, 67% and 33% COC water treatments. Concentrations in the control samples were similar to the treatment samples, therefore phenol is considered to be naturally occurring in the roots and tops of black willow. The other COCs, acetophenone, α, α-DMBA, and α-methylstyrene, were not detected in the roots and tops of any black willow specimens.

Based on the above, none or virtually none of the COCs were present in the plant tissue at the end of the pilot study. Tentatively identified compounds (TICs) and possible COC metabolites are discussed later in this report.

Media Final Sampling

Results for the final soil (media) sampling in March/April 2007 are provided in the Appendix in Table AB.2. No COCs were detected in the media of black willow, eastern red cedar and water oak species. Spruce pine specimens were not sampled for analysis of COCs as discussed previously.

No COCs were detected in the media for bald cypress with the following exception. Phenol was detected in one control samples at 0.108mg/kg and in one of the 33% COC water treatment samples at 0.0837mg/kg. Phenol in the media is not considered to be a metabolite of the COCs since it was also present in a control sample.

Tentatively Identified Compounds (TICs)

The TIC tables for plant tissue are provided in the Appendix. The evaluation of TICs was performed by LSU and PSI. The TICs in the treatment plant tissue were compared to those TICs found in the control plant tissue. Any TICs found in both treatment and control plant tissue at comparable concentrations were not included in these tables, as a compound found in the control samples is unlikely to be a metabolite of one of the constituents of concern. Additionally, TICs under 0.10mg/kg were not included in the TIC tables. TICs under 0.10mg/kg are below the level of detection for the COCs. Any TICs that are labeled as "unknown" in the TIC tables have a Quality Value < 75%. Compounds with quality values <75% cannot be used to accurately identify the TIC. The tables are broken down by plant species, tops and roots, and VOCs and SVOCs.

The metabolites of cumene and 4-cumylphenol involve the target compound COCs that were specifically tested for and were not found in the plant tissue. The primary focus of TIC evaluation by LSU and PSI was on possible metabolites of 4-cumylphenol, $C_{15}H_{16}O$. Therefore, TICs having more than 15 carbons were largely ignored since 4-cumylphenol would not

necessarily produce a larger compound during breakdown and because many naturally occurring larger hydrocarbons TICs appear to be present in plant tissue. The primary metabolites of 4-cumylphenol are α- methylstyrene and phenol. Alpha-methylstyrene has a molecular weight of 118.18 g/mol (Science Lab.com, 2008); phenol has a molecular weight of 94.11g/mol (Library 4 Science, 2005). Because both of the primary metabolites of 4-cumylphenol have smaller molecular weights than the parent compound, it was presumed that any other metabolites would also have comparative or smaller molecular weights than 4-cumylphenol. In addition to molecular weight, TICs not having the aromatic ring structure similar to the COC's, such as straight-chain hydrocarbons and cyclo-hydrocarbons, were considered to be naturally occurring in trees. Many smaller compounds, such as benzyl alcohol, phenylethyl alcohol and 2-hydroxybenzaldehyde, were detected as TICs during baseline sampling of plant tissue.

No large amount of any one TIC thought to be related to cumene or 4-cumylphenol breakdown was found in plant tissue. The following are TICs for plant tissue that may be related since they were not found in final sampling controls or in the baseline plant tissue samples. These are considered only as possibilities and not confirmed metabolites, since they could also be naturally occurring given the low concentrations observed.

- 4-(1-methylethyl)-phenol ($C_9H_{12}O$) found in: eastern red cedar roots – 100% (maximum = 6.0mg/kg)
- 3,4-dimethoxy-phenol ($C_8H_{10}O_3$) found in: bald cypress tops - 67% (maximum = 0.98mg/kg)
- 4-(3-hydroxy-1-propenyl)-phenol ($C_9H_{10}O_2$) found in: bald cypress tops - 67% (maximum = 1.1mg/kg)

The first TIC listed above is interesting because of its chemical structure relative to 4-cumylphenol. However, the relative concentration of this TIC represents only approximately 3%

of the 4-cumylphenol mass that was introduced to the trough. Therefore, it still does not represent a notable metabolite, and the other TICs at smaller concentrations are even less notable.

The TIC tables for soil (potting media) are provided in the Appendix. The evaluation of TICs was performed by LSU and PSI. The TICs in the treatment soil were compared to those TICs found in the control soil. Other evaluation procedures were similar to those described above for plant tissue. No TIC thought to be related to cumene or 4-cumylphenol breakdown was found in treatment soil. The TICs listed are primarily straight-chain hydrocarbons that would be expected with a peat-based potting media.

Sludge Sample Data

Because cumene and 4-cumylphenol were not detected in notable concentrations in the tree root or shoot tissue, the soil, or sludge, a combination of soil from well water, soil from pots, and decaying plant tissue such as roots, located in the bottoms of hydroponic troughs was sampled. Sludge was removed from each individual trough, totaling 40 samples.

Relatively small amounts of cumene and 4-cumylphenol were found in the sludge. The original sludge samples weighed less than 10 grams each. The highest mean concentration of cumene in each sludge sample was found in the 100% COC water troughs at a mean concentration of 0.001mg/kg. The highest mean concentration of 4-cumylphenol in sludge was found in the 33% COC water troughs at a mean concentration of 0.007mg/kg. Cumene and 4-cumylphenol were added to the hydroponic greenhouse system at mean mass amounts of 99.9 and 236.4 mg, 76.8 and 84.1mg, and 37.1 and 35.7 mg in the 100%, 67%, and 33% chemical water treatments respectively. These COCs were not found in the trough discharge water, plant tissue both roots and shoots, and potting soil. The cumene and 4-cumylphenol in the sludge accounts for a negligible amount of the mass added to the hydroponic greenhouse system.

Because cumene is slightly volatile, some of the input cumene may have been lost by volatilization between storage of the treatment water and running it through the hydroponic system. However, 4-cumylphenol is labeled as a SVOC and is not likely to have been lost by means of volatilization. The pilot study indicated that black willow, bald cypress, and water oaks are tolerable of both the chemical and salinity levels in the contaminated groundwater plume.

Final Nutrition Samples

Final nutrition samples were analyzed for the spruce pine trees. The analyzed minerals were B, Ca, Fe, Cu, Mg, Mn, P, K, Na, S, and Zn. Four replications of spruce pine from each water treatment were analyzed for mineral deficiencies. The replications were further divided into roots and tops. Roots were divided from tops and analyzed separately. Roots were washed with DI water to remove soil. Roots and tops were dried in an oven. After grinding, the samples were sent to the LSU Agriculture Chemistry lab for nutritional analysis using ICP Group 1.Spruce pine in all water treatments were sampled because of their low survival rates. The purpose of the nutrient sampling in all water treatments of spruce pine was to determine if the poor health of spruce pine trees was attributed to nutrient deficiencies. The other tree species did not have as severe mortality rates nor did they receive as poor visual ratings as the spruce pine species did. Table 9 displays mean concentrations of nutrients in the spruce pine roots. Table 10 displays the mean concentrations of nutrients in spruce pine tops.

Calcium concentration (%) in the 100% NaCl water and 100% COC water treatment waters were significantly higher ($p \leq 0.005$) than calcium levels in the DI water. However, the Ca concentrations of spruce pines are within the sufficiency levels (>0.29%) reported by BFW, 2005.

Table 9. Mean Concentration of Minerals in Spruce Pine Roots

Mineral	Water Treatment						
	DI	**100% NaCl**	**50% NaCl**	**100% COC**	**67% COC**	**33% COC**	**Sig.**
B	16[Z]	16.9	22.2	26.65	20.68	16.93	NS
Ca	0.33C	0.56A	0.37BC	0.47AB	0.37BC	0.38BC	**
Cu	11.09	13.96	14.09	16.05	9.27	9.85	NS
Fe	404ABC	586.3ABC	640.0AB	769.8A	271.0C	355.0BC	*
Mg	0.14B	0.25A	0.15B	0.15B	0.16B	0.17B	*
Mn	138.00	263.28	139.5	243.0	112.4	122.00	NS
P	0.12	0.10	0.10	0.11	0.09	0.12	NS
K	0.45	0.20	0.24	0.35	0.26	0.37	NS
Na	0.23	0.38	0.21	0.19	0.26	0.30	NS
S	0.12	0.16	0.12	0.12	0.11	0.14	NS
Zn	55.43	69.2	49.1	84.05	36.4	177.6	NS

[Z] Means across rows with different letters are significantly different by * p≤0.05; NS = not significant. Sig = Significance. B= boron, Ca= calcium, Cu= copper, Fe= iron, Mg= magnesium, Mn= Manganese, P= phosphorous, K= potassium, Na= sodium, S= sulfur, and Zn= zinc. Means were generated using a PROC GLM SAS program and duncans.

Iron concentrations (mg/kg) were not significantly different between the DI water treatment and any other water treatment. However, there was a significant difference in iron concentrations between 100% COC and 67% COC ($p \leq 0.05$) water treatments and the 100% COC and the 33% COC ($p \leq 0.05$) water treatment. The mean Fe concentration of spruce pine roots in all water treatments was higher than the reported sufficiency range of 30-180mg/kg (BFW, 2005).

The Mg concentration in spruce pine roots growing in the 100% COC water treatment had a significantly higher concentration of Mg ($p \leq 0.005$) than all other water treatments. BFW, 2005 reports a sufficiency range for Mg concentrations in pines at >0.06%. All of the water treatments were in this range.

Spruce pine tops growing in the 100% COC water treatment had a significantly higher concentration ($p \leq 0.05$) of B than spruce pine tops growing in all other water treatments with the exception of the 50% NaCl water treatment. Spruce pine tops growing in the 100% COC water

treatment and 50% NaCl water treatment had significantly higher ($p \leq 0.05$) concentrations of B than the DI water treatment. B sufficiency ranges were not reported for spruce pine trees.

Table 10. Mean Concentration of Minerals in Spruce Pine Tops

	Water Treatment						
Mineral	**DI**	**100% NaCl**	**50% NaCl**	**100% COC**	**67% COC**	**33% COC**	**Sig.**
B	16.35C[Z]	20.05BC	28.43AB	33.90A	21.38BC	19.23BC	*
Ca	0.39B	0.52AB	0.61AB	0.84A	0.33B	0.44B	*
Cu	9.92A	7.62B	7.07B	7.39B	6.09B	7.51B	*
Fe	205.50AB	226.00A	158.50AB	227.00A	131.75B	207.50AB	*
Mg	0.12B	0.25AB	0.36AB	0.48A	0.13B	0.15B	*
Mn	264.50	162.13	236.98	266.70	181.50	234.75	NS
P	0.11	0.11	0.10	0.11	0.10	0.12	NS
K	0.58	0.64	0.84	0.81	0.59	0.67	NS
Na	0.38	0.92	0.87	0.97	0.35	0.55	NS
S	0.14	0.18	0.22	0.23	0.11	0.14	NS
Zn	82.48	122.30	75.78	66.90	50.15	153.35	NS

[Z] Means across rows with different letters are significantly different by *;NS = not significant. Sig. = Significance. B= boron, Ca= calcium, Cu= copper, Fe= iron, Mg= magnesium, Mn= Manganese, P= phosphorous, K= potassium, Na= sodium, S= sulfur, and Zn= zinc. Means were generated using a PROC GLM SAS program and duncans.

Spruce pine tops growing in the 100% COC water treatment had a significantly higher concentration ($p \leq 0.05$) of Ca than the spruce pine tops growing in the 67% COC water treatment, 33% COC water treatment, and DI water treatments.

Spruce pine tops growing in the DI water treatment had a significantly higher ($p \leq 0.05$) concentration of Cu than all other water treatments. However the spruce pine top samples all had Ca concentrations within the reported sufficiency range of >0.29% (BFW, 2005).

Spruce pine tops growing in the 67% COC water treatment had a significantly lower ($p \leq 0.05$) concentration of Fe than all other water treatments. However it fell within the reported sufficiency range of 30-180mg/kg Fe concentration. The 50% NaCl treated spruce pines did as well. All other spruce pine mean concentrations of Fe were above the sufficiency range (BFW, 2005).

Spruce pine tops growing in the 100% COC water treatment had a significantly higher ($p \leq 0.05$) concentration of Mg than spruce pine tops growing in the 67% COC, 33% COC, and DI water treatments. All Mg concentrations of spruce pine tops were within the sufficiency range reported by BFW, 2005 of >0.06%.

Tissue samples from the spruce pine trees were not severely limited in any of the nutrients with the exceptions of shoot tissue low in Fe. Although most nutrition concentrations were within the reported levels of minerals for pine trees, there was likely another cause for the high mortality rates of spruce pines. The most probable cause of the poor spruce pine health was poor nursery quality stock at the beginning of the study. The spruce pines were purchased as bare root seedlings and most likely had been held too long without soil and water before LSU obtained them, thus weakening them.

CHAPTER 5

SECOND PILOT STUDY RESULTS (2007-2008)

RESULTS –SECOND GREENHOUSE PILOT STUDY

Environmental Conditions

Temperature

Greenhouse temperatures were recorded electronically each hour with a HOBO data logger. Temperature was also recorded manually using a high low thermometer each time the greenhouse was visited, approximately one to two times week. Figure 10 depicts the high and low temperatures in the greenhouse during the study.

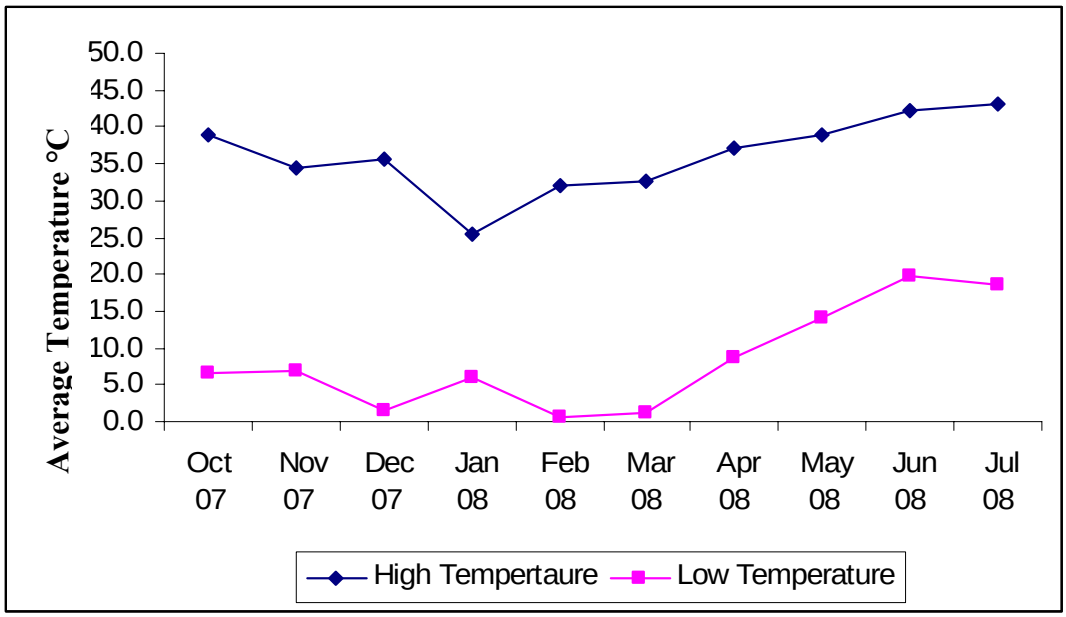

Figure 10. Average Greenhouse Temperature 2007-2008

Relative Humidity

Relative humidity is an additional environmental factor that plays a role in plant growth. Figure 11 depicts the average relative humidity in the greenhouse during the nine-month study. Relative humidity was electronically recorded using a HOBO data logger hourly through the study.

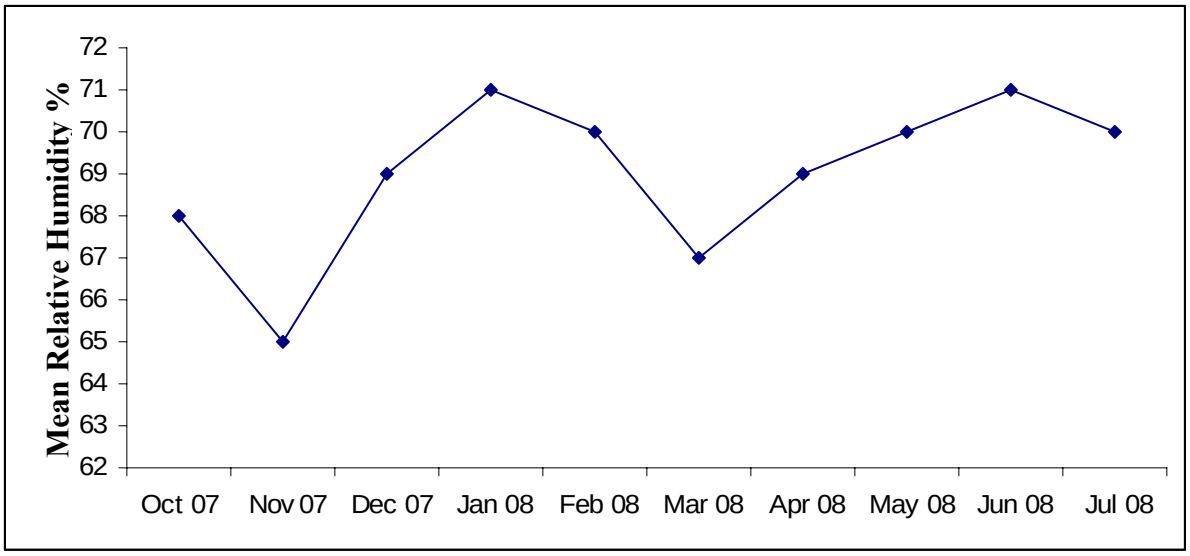

Figure 11. Average Percent Relative Humidity 2007-2008

Water Monitoring

Treatment water was spiked weekly with the three treatments:

1. Control: deionized water only
2. Low: 0.5µg/mL cumene + 2µg/mL 4-cumylphenol
3. High: 1µg/mL cumene + 4µg/mL 4-cumylphenol

Monthly, input samples were taken from individual troughs. The amount of COC's present in samples was analyzed and considered the initial concentration. Concluding the week, the same troughs were sampled again. The samples were analyzed for COC's. The remaining amount of COC's at the end of the week was considered the discharged concentration. Subtracting the discharge concentration from the initial concentration gave the amount of chemicals potentially utilized by the tree. The differing amount is the potentially remediated amount of chemicals. Removal of constituents was hypothesized to be through translocation by the tree, diffusion into the soil, or diffusion through the soil into the atmosphere.

Table 11 displays the mass of cumene and 4-cumylphenol added to the treatment water. The total mass of target compounds added to the hydroponic system was determined by several

calculations. First, the initial volume of water in each trough was multiplied by the mass of cumene or 4-cumylphenol added. Second, the discharge volume of water in each trough was multiplied by the mass of cumene or 4-cumylphenol discharged from the trough. Third, the second answer was subtracted from the first answer. The subtraction gave the mass of the constituents in the water that was added and not discharged from the troughs. The discharge values were taken once a month. For all other discharge values an average of that months discharge was used in order to determine the final mass added to the system.

Table 11. Mass of Cumene and 4-Cumylphenol Added to the Treatment Water

		Volume of Water Added to Trough		Constituent Mass in Water Added	
Block	**Water Treatment**	**(gal)**	**(liters)**	**4-cumylphenol (mg)**	**Cumene (mg)**
I	**Low**	166.5	630.3	895.8	212.5
II	**Low**	177.5	671.9	917.9	222.0
III	**Low**	170.2	644.2	899.7	210.5
I	**High**	161.3	611.3	1793.1	443.0
II	**High**	177.5	671.9	1802.0	438.1
III	**High**	177.8	672.9	1858.2	427.2

Low = 0.5µg/mL cumene + 2µg/mL 4-cumylphenol; High = 1µg/mL cumene + 4µg/mL 4-cumylphenol

Average Water Use for Trees Exposed to Contaminated Water

Water usage was monitored weekly. Input and discharge levels were recorded for all individual troughs. Table 12 gives the water usage of individual troughs by treatment. Each trough included three trees, one of each species. The data indicate that trees in the DI (control water) treatment used on average more water than trees growing in the high water treatment $p \leq 0.006$. There were no statistical differences between the DI and low water treatment and the low and high water treatments. Data were analyzed using a Proc Mixed SAS program and Saxton's Macro.

Table 12. Average Water Use (Liters/Day) for Individual Troughs by Water Treatment

Water Trt.	Liters/Day	Water Trt.	Liters/Day	Significance
DI	1.743	Low	1.585	N.S.
DI	1.743	High	1.383	**
Low	1.585	High	1.383	N.S.

Numbers across rows with ** are statistically significant at p≤0.006. N.S. = not significant.

Average Water Use for Trees in Non-Contaminated Water

The back portion of the greenhouse was dedicated to determining water usage by individual species. Water levels were recorded weekly and later biweekly in warmer months to determine which tree species used the largest amount of water. Individual troughs held five trees. All five trees were the same species. There were three troughs (fifteen trees) represented for each species. Table 13 displays water usage by species. The data indicates that the troughs with black willow trees used more water than any other species. Cottonwood trees were the second highest water use species. There was no statistical difference in water use between the bald cypress, eastern red cedar, and water oak trees. A Proc Mixed SAS program and Saxton's macro were used to statistically analyze the data.

Table 13. Water Usage by Tree Species

Species	Average Daily Water Use (liters)
Black willow	1.287A
Cottonwood	0.9464B
Eastern red cedar	0.6435C
Bald cypress	0.5299CD
Water oak	0.3407D

Values in columns with different letters are statistically significant at p≤0.0001

Data in Table 14 represent average water used per trough throughout the study. It is important to note that the black willow trees were substantially larger than the other tree species by the end of the study. Larger trees naturally use greater quantities of water compared to smaller trees. Although all trees began the study roughly the same in size, the black willows grew at faster rates than the other species. Conger and Portier, 2001 conducted research on two black willow plots. The black willows were growing over a shallow groundwater plume contaminated

with the herbicide Bentazon. During sampling periods in 1998 and 1999 the black willows in the study had an average daily water use between 6 to 13L/day/m^3. While other literature indicates that black willows are heavy water users the literature does not report quantity of water used. The black willows in Conger and Portier's study had higher daily averages than those in our study. The trees in their study were planted in the field. The black willows in this study were limited in size by the containers. All trees continued using water throughout the study. Even in colder months, the trees translocated water. The ability to use water in dormant periods is important to the hydraulic control of the plume water.

Table 14. Monthly Average Water Usage (Liters/Day) for each Species

Species	Month								
	Oct	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**
BC	0.416	0.303	0.341	0.265	0.303	0.379	0.492	0.946	1.363
BW	1.059	1.098	0.946	0.568	0.492	0.681	1.589	3.975	2.763
CW	n.a.	0.227	0.303	0.303	0.379	0.606	0.984	2.006	2.233
ERC	1.022	0.492	0.416	0.341	0.303	0.492	0.719	0.871	1.135
WO	0.416	0.341	0.303	0.227	0.114	0.189	0.378	0.454	0.606

BC = bald cypress, BW = black willow, CW = cottonwood, ERC= eastern red cedar, WO= water oak. Sp. = species.

Plant Quality

COC Subjected Trees

Several growth attributes were monitored throughout the study. Tree height, caliper, and visual ratings were measured to determine if the COC's present in the water treatments had an impact on tree growth. The trees growing in DI water represent normal growth of the species. Comparing the trees growing in the DI water to trees growing in the low and high water treatments determines if any negative growth effects occurred because of the presence of the COC's. Trees were compared within species only.

Height

Figure 12 gives the average heights of the bald cypress tree species throughout the nine-month study. Growth rapidly increased beginning in March and was most likely a results of the warmer weather. Bald cypress growing in all three water treatments, DI, low, and high, grew significantly from the start (Oct) to the end (June) of the greenhouse study $p \leq 0.0001$. Bald cypress in the DI water treatment had an average height of 0.352m in October and was measured again, just before harvest at 0.937m. Bald cypress growing in the low water treatment had average heights of 0.395m and grew to an average height of 0.862m at the end of the study. Cypress growing in the high water treatment had an average height of 0.357m and grew to 0.847m by the end of the study. Statistical analysis was conducted on the heights of the bald cypress in June. There were no significant differences between the heights of bald cypress growing in the DI, low or high water treatments. The averages and significances were determined by using a PROC Mixed SAS program accompanied by Saxton's Macro. Differences reported are of Least Squares Means.

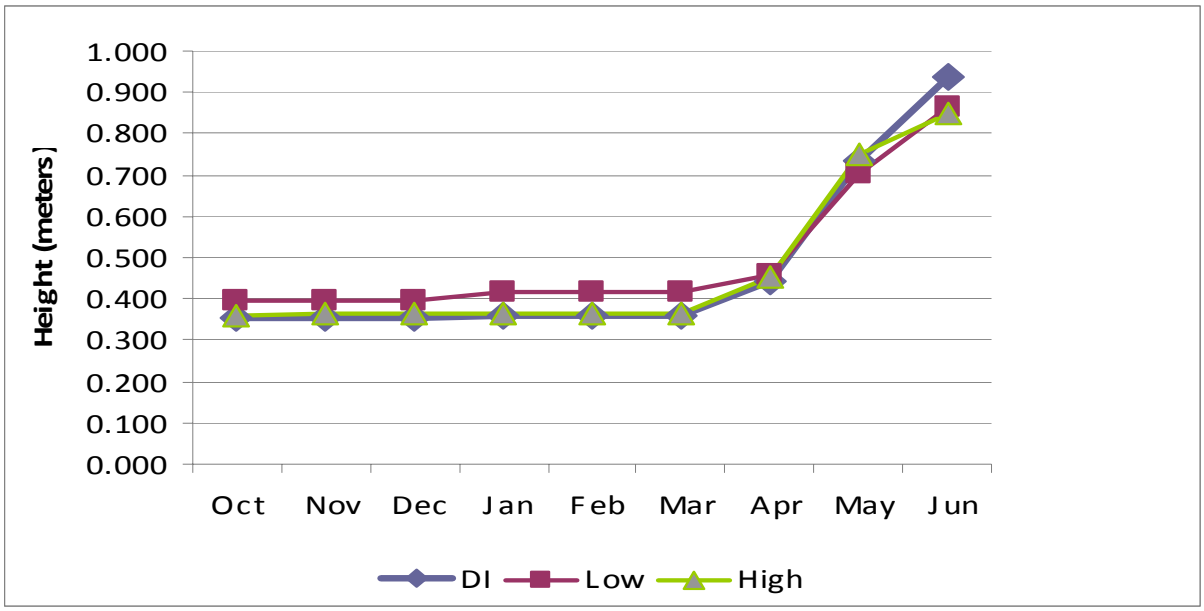

Figure 12. Average Height of Bald Cypress (m)

Figure 13 displays the average heights of the black willows throughout the greenhouse study. Black willows growing in all three water treatments, DI, low, and high, grew significantly from the start (Oct) to the end (June) of the greenhouse study $p \leq 0.0001$. Black willows growing in the DI water treatment had average heights of 0.820m in October and grew to average heights of 3.75m by the end of the greenhouse study. Black willows growing in the low water treatment started with average heights of 0.760m and completed the greenhouse study with average heights of 4.12m. Black willows growing in the high water treatment began the study with average heights of 0.83m and finished the study with average heights of 4.14m. Low water treatment black willows (4.12m) had significantly greater ($p \leq 0.0211$) heights than DI water treatment black willows (3.75m). High water treatment black willows (4.14m) also had significantly greater ($p \leq 0.0166$) heights than DI water treatment black willows (3.75m). Black willows growing in the contaminated water grew better than black willows in regular DI water. The averages and significances were determined by using a PROC Mixed SAS program accompanied by Saxton's Macro. Differences reported are of Least Squares Means.

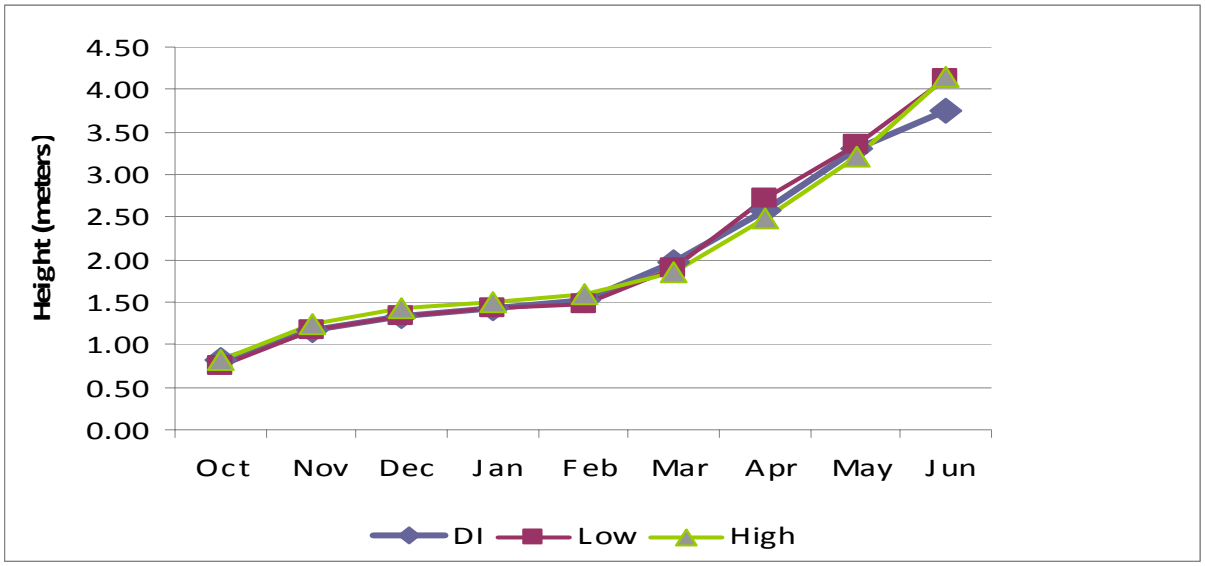

Figure 13. Average Height of Black Willow (m)

Figure 14 displays the average heights of the cottonwood trees throughout the greenhouse study. Cottonwoods growing in all three water treatments, DI, low, and high, grew significantly from the start (Oct) to the end (June) of the greenhouse study $p \leq 0.0001$. Cottonwoods growing in the DI water treatment began the study with average heights of 0.357m and concluded the study with average heights of 1.10m. Cottonwood trees growing in the low water treatment had average heights of 0.34m at the beginning of the study and concluded the study with average heights of 1.20m. Heights of cottonwood trees growing in the high water treatment averaged 0.32m at the beginning of the study and 1.10m at the end of the study. There were no significant differences between heights of cottonwood trees growing in the differing water treatments. The averages and significances were determined by using a PROC Mixed SAS program accompanied by Saxton's Macro. Differences reported are of Least Squares Means.

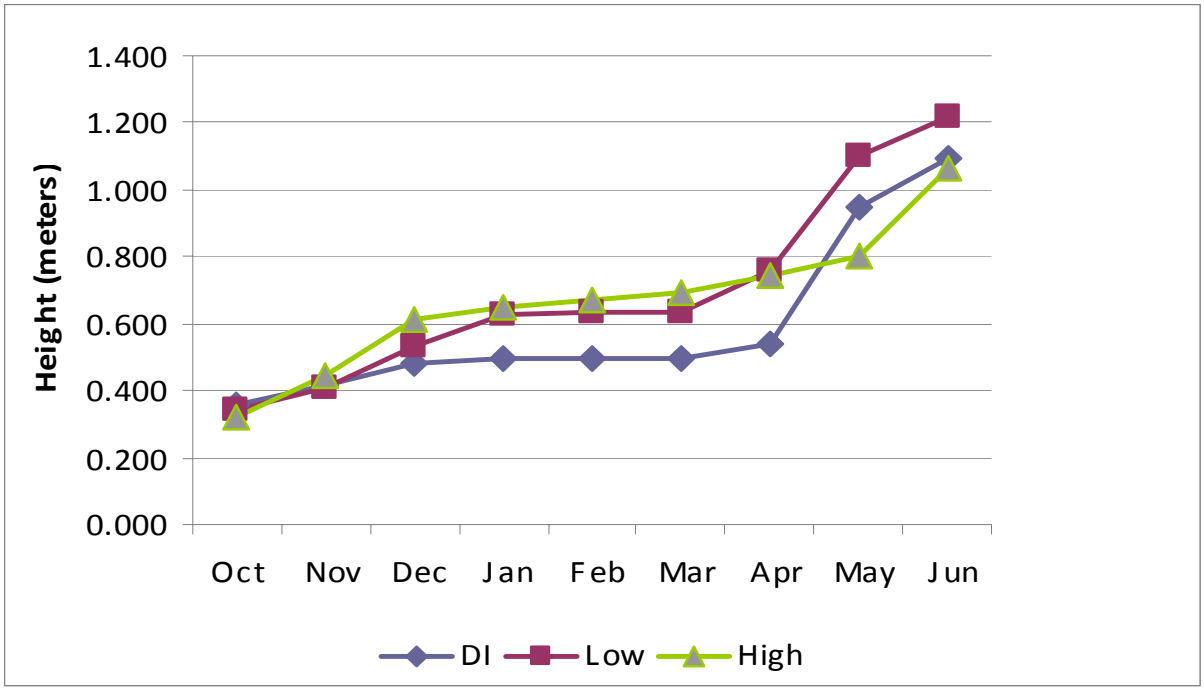

Figure 14. Average Height of Cottonwood (m)

Figures 12-14 show the average heights of all three-tree species in all three water treatments throughout the greenhouse study. The graphs coupled with statistical analysis show

that the chemical water treatments did not have any negative effects on growth of the three tree species. The black willows grew significantly taller when subjected to the water treatments. The chemicals may act as a stimulus for increasing height in black willows at low concentrations.

Caliper

Figures 15, 16, and 17 give the mean caliper measurements for each tree species by treatment and month. The averages and significances were determined by using a PROC Mixed SAS program accompanied by Saxton's Macro. Differences reported are of Least Squares Means. All tree species in all treatments grew significantly in caliper measurements between the months of October and June ($p \leq 0.0001$). Caliper measurements are reported in mm.

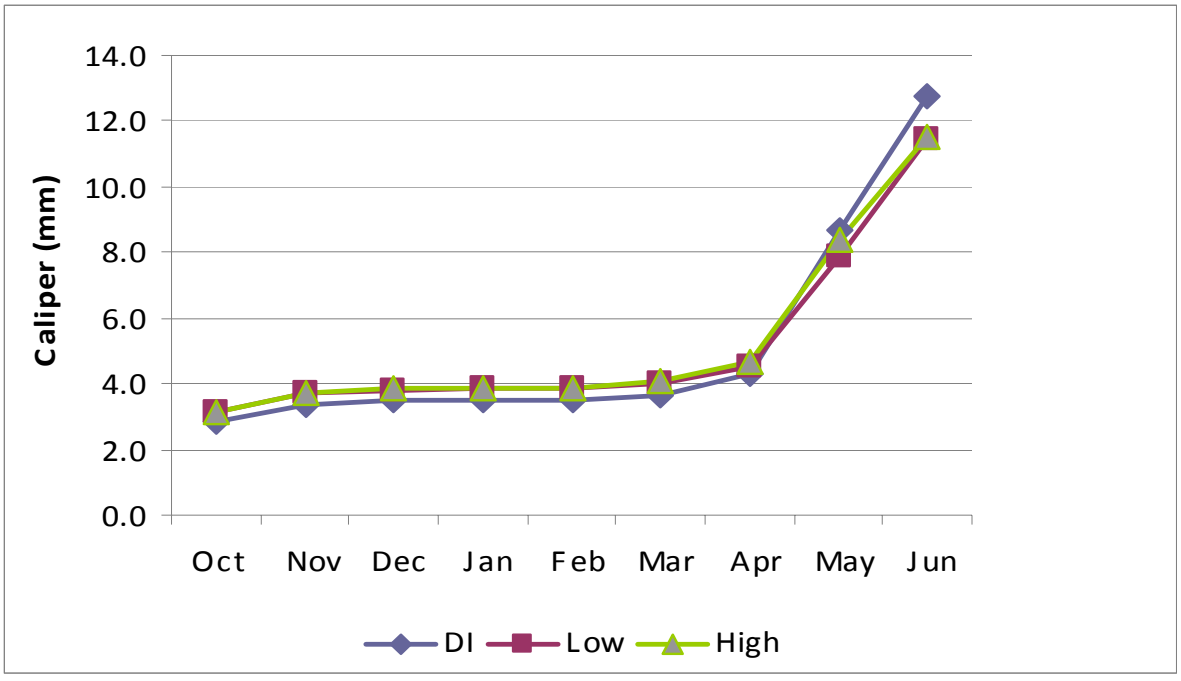

Figure 15. Average Caliper Bald Cypress (mm)

Caliper dimensions of the bald cypress trees started substantually increasing in March. The calipers rapidly increased from March to June. Most importantly, the calipers of all bald cypress growing in all three water treatments significantly increased ($p \leq 0.0001$) from October to June. The bald cypress growing in the DI water treatmenmts began the study with average caliper measurements of 2.8mm and ended the study with average measurements of 12.7mm.

The cypress growing in the low water treatment increased average caliper measurements from 3.2 to 11.5mm and those cypress growing in the high water treatment had average increses in caliper measurements from 3.1mm to 11.5mm by the end of the study. While final caliper measurement of the bald cypress trees were greatest in the DI water treatment, there were no statistical differences between final measurements of bald cypress calipers growing in the DI , low, or high water treaments. This finding indicates that bald cypress are not negitvely affected when growing in the chemically contaminated water.Figure 16 displays the mean caliper measurements for the black willow tree species.

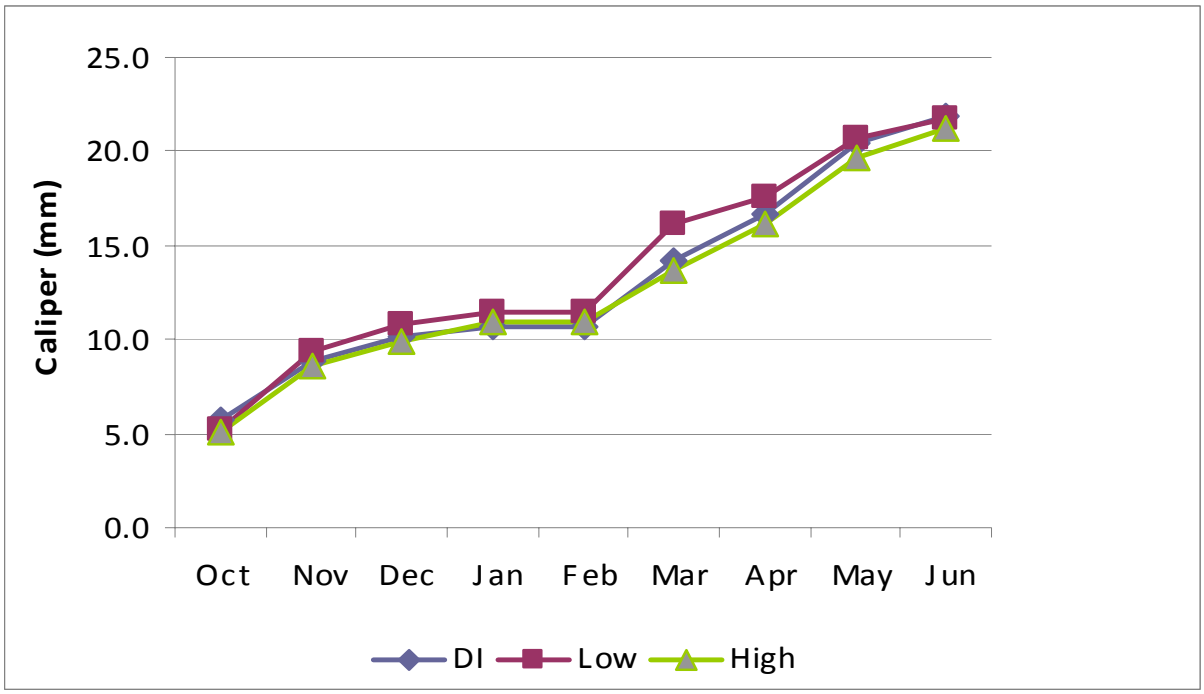

Figure 16. Average Caliper Black Willow (mm)

Caliper measurements of the black willow trees began to substantially increase in February. They continued to rapidly grow through the completion of the greenhouse study. Black willows growing in all water treatments significantly increased in caliper from October to June $p \leq 0.0001$. Black willows growing in the DI water treatment increased average caliper from 5.62mm to 21.76mm by the end of the study. Black willows growing in the low water treatment

increased average caliper measurements from 5.30mm to 21.86mm by the end of the study. Black willow trees growing in the high water treatment increased average caliper measurements from 5.07mm to 21.23mm at the end of the study. There were no statistical differences between final caliper measurements of black willows growing in the DI, low and high water treatments. Similar to the bald cypress, the black willows did not suffer any negative caliper effects when subjected to chemically contaminated water. Figure 17 displays the mean caliper measurements for the cottonwood species by water treatments.

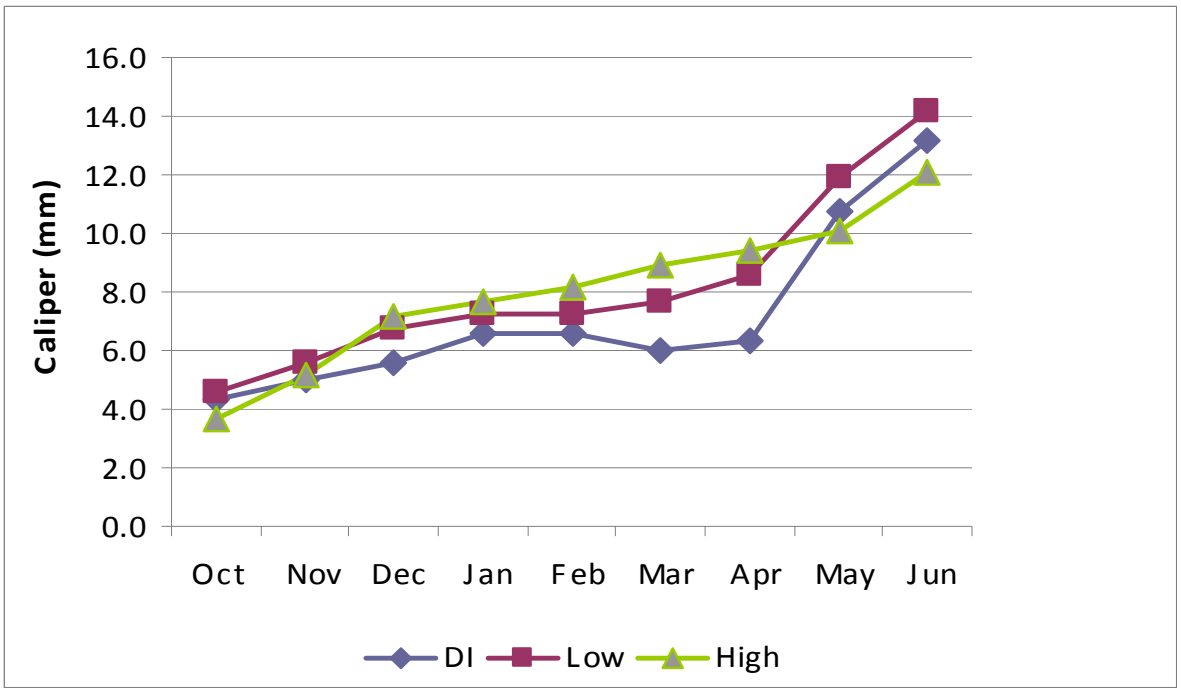

Figure 17. Average Caliper Cottonwood (mm)

The cottonwood trees had a continued increase in caliper measurement throughout the study. Rapid growth began in April. All cottonwood trees increased their mean caliper measurements from October to June ($p \leq 0.0001$). Cottonwoods growing in the DI water treatment grew from 4.3mm in October to 13.1mm in June. The cottonwood trees growing in the low water treatment increased caliper measurements from 4.7mm in October to 14.2mm in June. The cottonwood trees growing in the high water treatment increased caliper measurements from

3.6mm in October to 12.1mm in June. Statistical analysis of the June caliper measurements indicated no significant differences in caliper size of cottonwood trees growing in the three water treatments. As was the case for bald cypress, and black willow species, the cottonwoods caliper growth was not negatively affected when subjected to chemically contaminated water.

Visual Rating

Visual ratings were taken on a scale of 1 to 6; 1 representing all brown or no leaves, 3 representing half alive and half dead leaves, and 6 representing completely alive and green leaves. It is expected for the deciduous trees to have visual ratings of 1 or 2 in winter months. These lower winter ratings were not indications of chemical effect on tree health. Figures 18-20 give the mean visual rate for each tree species by treatment and month.

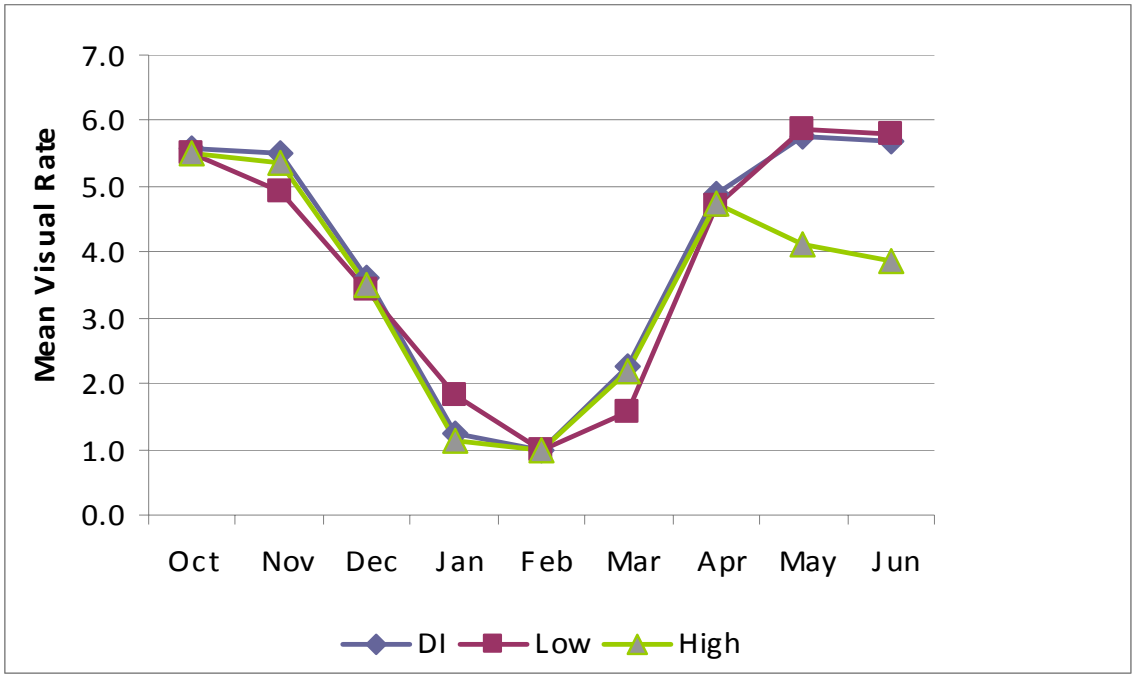

Figure 18. Mean Visual Rating for Bald Cypress

Bald cypresses are deciduous trees. In months January, February, and March the lower scores reflect the loss of leaves as a result of weather changes. Bald cypress in the DI and Low water treatments regained their leaves and green color by the end of the study. The visual ratings for both the DI and Low water treatments were slightly higher at the end of the study in June

compared to October. The bald cypress in the high water treatment had budding and leaf emergence, but after April, the mean visual rating began to decline. In April, all but two of the bald cypress in the high water treatment had perfect visual scores (6.0), the two that did not were dead (1.0). In May, one of the bald cypress died; therefore it went from a visual rating of 6.0 to 1.0 and remained so in June. In the last two months of the study, three of the eight bald cypresses were dead. Two of those were receiving low visual scores since January, the other since May.

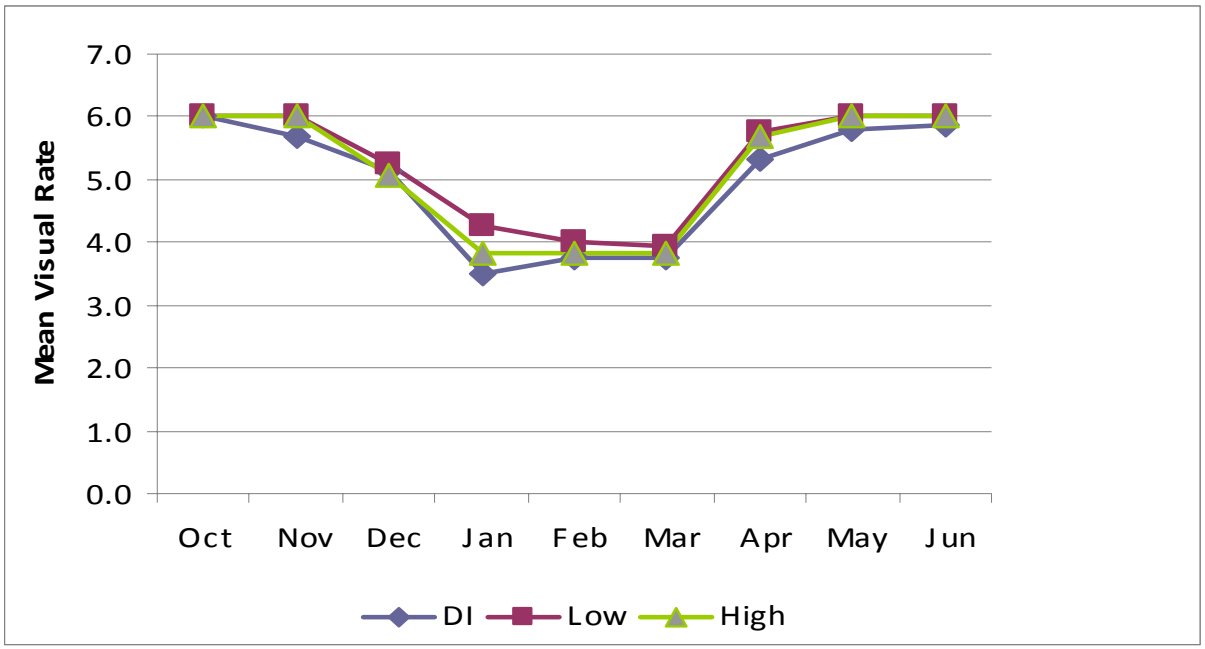

Figure 19. Mean Visual Rating for Black Willow

Black willows are decidious trees. Low visual scores were given in January, February, and March because the trees defoliated. The black willow trees did not lose all their leaves during the colder months like the bald cypress did. Black willows in all water treatments had visual scores equal to that with which they began the study.

Cottonwood trees are decidious trees. Lower visual ratings were given in January, Febrary, and March when the temperatures were cooler and the trees were losing their leaves. Like the black willow, the cottonwood trees did not lose 100% of their leaves during the winter. Visual ratings started rising in April and continued to do so for those cottonwood trees growing

in the DI water treatment. The visual ratings declined for cottonwood trees growing in the low and high water treatments. One cottonwood tree in both the low water and high water treatments died during May. All other cottonwood trees in the low and high water treatments were slowly declining in visual color.

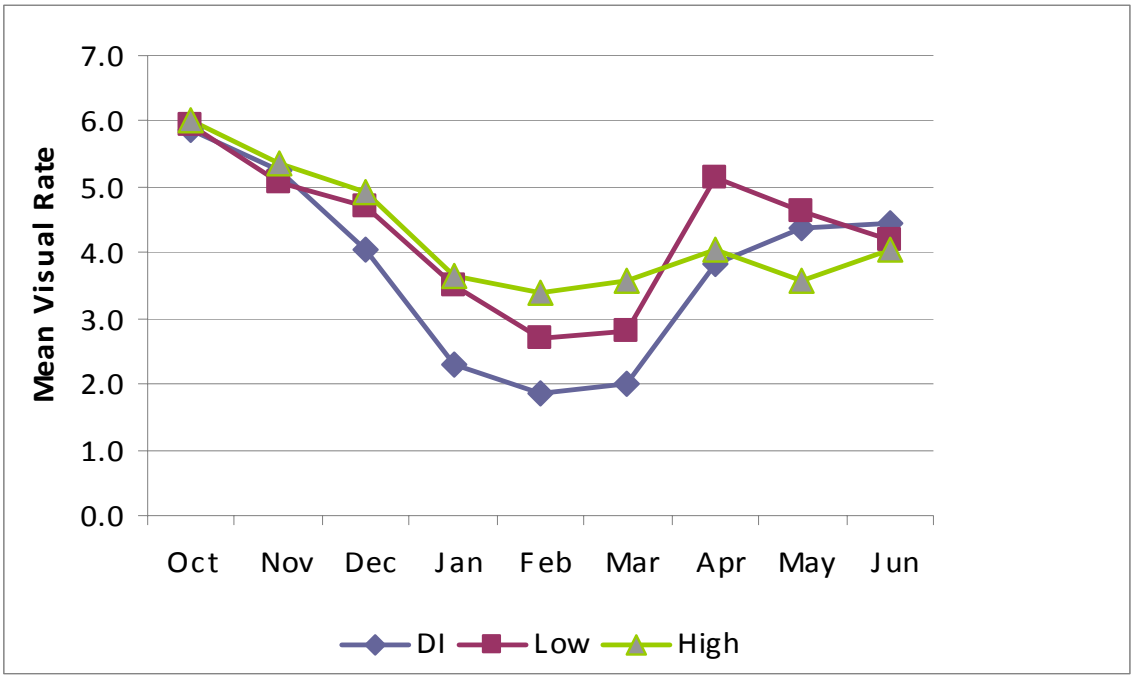

Figure 20. Mean Visual Rating for Cottonwood

Table 15 gives the statistical differences in individual species between water treatments.

Table 15. Average Visual Rating of Tree Species by Month and Treatment

Species	Water Treatment	October Visual	June Visual	Significance
Bald cypress	DI	5.56[Z]	5.69	NS
Bald cypress	Low	5.50	5.81	NS
Bald cypress	High	5.50	3.88	**
Black willow	DI	6.00	5.88	NS
Black willow	Low	6.00	6.00	NS
Black willow	High	6.00	6.00	NS
Cottonwood	DI	5.88	4.44	**
Cottonwood	Low	5.94	4.19	**
Cottonwood	High	6.00	4.06	**

[Z] Values across rows with ** are significantly greater p≤0.005; NS = not significant.

There were no significant decreases in visual rating between the months of October and June for the bald cypress trees growing in DI and low water treatments. However, there was a

significant visual decrease in bald cypress trees growing in the high water treatment between October and June.

The high water treatment bald cypress trees were rated with slightly greater than 50% ratings on a visual scale. The bald cypress leaves had fully emerged from the winter months. Insects were not troublesome in the month of June nor were the bald cypress trees affected by drought in the early summer months. Therefore, it is concluded that at a constant high rate of chemical concentration in the water will impact the health of the bald cypress tree. However, the significant decrease from October to June was minimal changing only from an average of 5.5 to 3.88.

The black willow trees showed no decline in visual ratings between the months of October and June. This indicates that the black willow trees when subjected to low and high water treatments remain as healthy as black willows in uncontaminated (DI) water.

All cottonwood trees declined in visual ratings between the months of October and June. The significant decrease in leaf color may be attributed to chemical influences, since the low and high water treated cottonwoods were affected to a greater degree than the trees in the DI water treatment. However, since the DI treatment trees also significantly declined in visual ratings there may be other explanations such as a lack of fertilizer, or needing to be bumped up to a larger pot size. However, the black willows being larger than the cottonwood trees did not have a visual decrease in leaf color and were potted in the same size pots. The difference in species may result in different fertilizer requirements of trees. It should be noted that a 15-12-9 Osmocote 12-14 month fertilizer was applied at the beginning of the greenhouse experiment at the medium rate, which should have been adequate for the study.

Black willows proved to be the best candidate for remediation of the plume water based on visual ratings. The lack of a significant decrease in visual color indicates the species ability to

withstand a constant supply of contaminated water. Unlike the greenhouse study, trees planted over the plume, will not only use water from the plume. The majority of water is translocated from a tree's lateral roots during normal seasons. However if there is a drought, a tree will draw the majority of its water from its tap or deeper roots. The tap root system is the portion of the trees root that will be using the contaminated plume water. There will always be a contaminant dilution taken up by the tree. Whereas in this greenhouse study, the trees growing in the high level treatment were taking up the maximum-recorded levels of contaminants ever found in the plume water each week. Realistically, the trees growing in the field were represented with the low water treatment trees in this greenhouse study. However, during periods of drought, trees naturally take up a larger percentage of water from the tap root system. Using the visual ratings and based on the combination of water intake from the tap roots along with lateral roots, both the bald cypress and black willow trees can be recommended for full scale planting over the plume water.

Water Use Only Trees

Height

Figure 21 gives the average height of each species. Trees in the water usage study were located in the back portion of the greenhouse. Each trough had the five trees. All five trees in each trough were of the same species. These troughs were never spiked with chemically treated water. DI water was used as the water source for this portion of the study. The goal of this portion of the study was to determine which trees species used the largest amounts of water. This is important in determining hydrologic control of the plume water. The height averages and significances were determined by using a PROC Mixed SAS program accompanied by Saxton's Macro. Differences reported are Least Squares Means.

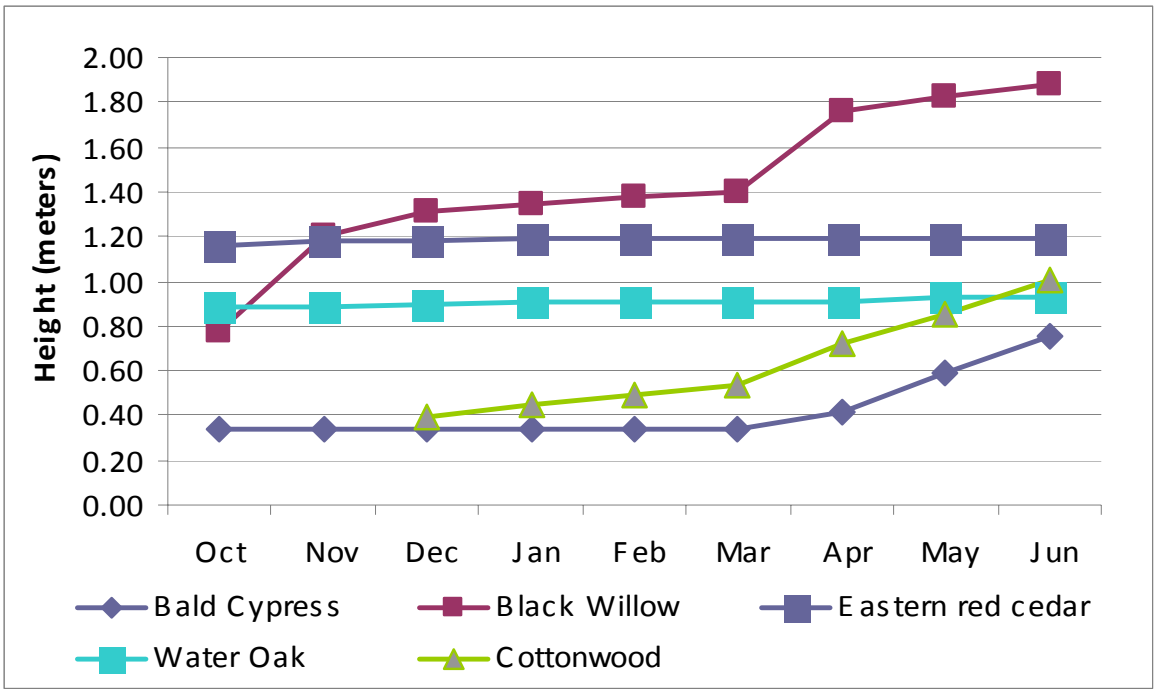

Figure 21. Average Height of Trees in the Water Use Experiment

There was never a point of significant growth for either the eastern red cedar or water oak trees throughout the study. These trees began the study as larger specimen than the other species. They were one year old seedlings. The limiting growth factor was most likely the fact that their roots were root bound in the pots after a few months of the study. Whereas, the other tree species were much smaller at the beginning of the study and were able to grow into the pots.

The roots of the other three tree species grew out of the pots and into the troughs. By the end of the study they needed to be bumped up to the next size pot, but were not constricted as their roots emerged from the pots. The bald cypress, cottonwood, and black willow trees had a rapid height increase in March. Table 16 displays the differences in mean heights between the months of October and June.

The bald cypress, black willow, and cottonwood trees all significantly increased in height between the months of October and June. The eastern red cedars and water oaks did not significantly increase in height. The bald cypress, black willows, and cottonwood species all

started out as small rooted cuttings, where as the eastern red cedar and water oak trees were larger rooted cuttings. The size difference may have actually prevented the eastern red cedars and water oaks from growing as much as the other test tree species. The difference may be attributed to the fact that all tree species were planted in trade gallon pots, so that they would fit in and not overwhelm the hydroponic system in which the trees grew. The larger trees may not have had enough space to continue growing as the smaller trees. It is important to note that the black willow trees grew to average heights of 1.88m in the same size pots as the eastern red cedars and water oaks. Comparing the June heights of species to one another, statistics indicated that the black willow trees species were taller than all other species by a factor of $p \leq 0.0001$. The bald cypress trees were significantly shorter than the cottonwood trees ($p \leq 0.0076$), the eastern red cedar trees ($p \leq 0.0001$), the water oak trees ($p \leq 0.0431$) and the black willows trees ($p \leq 0.0001$). The cottonwood trees were significantly shorter than the eastern red cedar trees ($p \leq 0.0413$). There was no significant difference in height between the cottonwood and water oak trees. The eastern red cedar trees were significantly taller than the water oak trees ($p \leq 0.0030$).

Table 16. Average Heights of Tree Species in the Water Use Experiment

Species	Oct Height (m)	June Height (m)	Significance
Bald cypress	0.34	0.76	***
Black willow	0.78	1.88	***
Cottonwood	0.40	1.00	***
Eastern red cedar	1.16	1.19	NS
Water oak	0.89	0.93	NS

Values across rows with * are significantly different by $p \leq 0.0001$; NS = not significant. Heights are reported in meters.**

Height differences occurred between species but there were varying starting heights between the species. Based on these findings the black willows are the largest of all tested species followed by the eastern red cedar, cottonwood, water oak, and the bald cypress trees in descending order of heights. Generally, a larger tree will use more water than a smaller tree. It is expected that the black willows being the tallest species also took up the largest amounts of

water. The ability to translocate large amounts of water suits the needs of this study because the more water that is translocated by the tree; the less contaminated water there is remaining in the plume. However, Georgia Gulf has strict security requirements making large trees less attractive to the area of interest because they may block the security cameras. Trees that can be easily pruned potentially hedged and have low litter rates are the most desirable for this area of interest.

Caliper

Figure 22 gives the average caliper measurement of each species over the nine month period. The averages and significances were determined by using a PROC Mixed SAS program accompanied by Saxton's Macro. Differences reported are Least Squares Means. Caliper measurements are reported in millimeters.

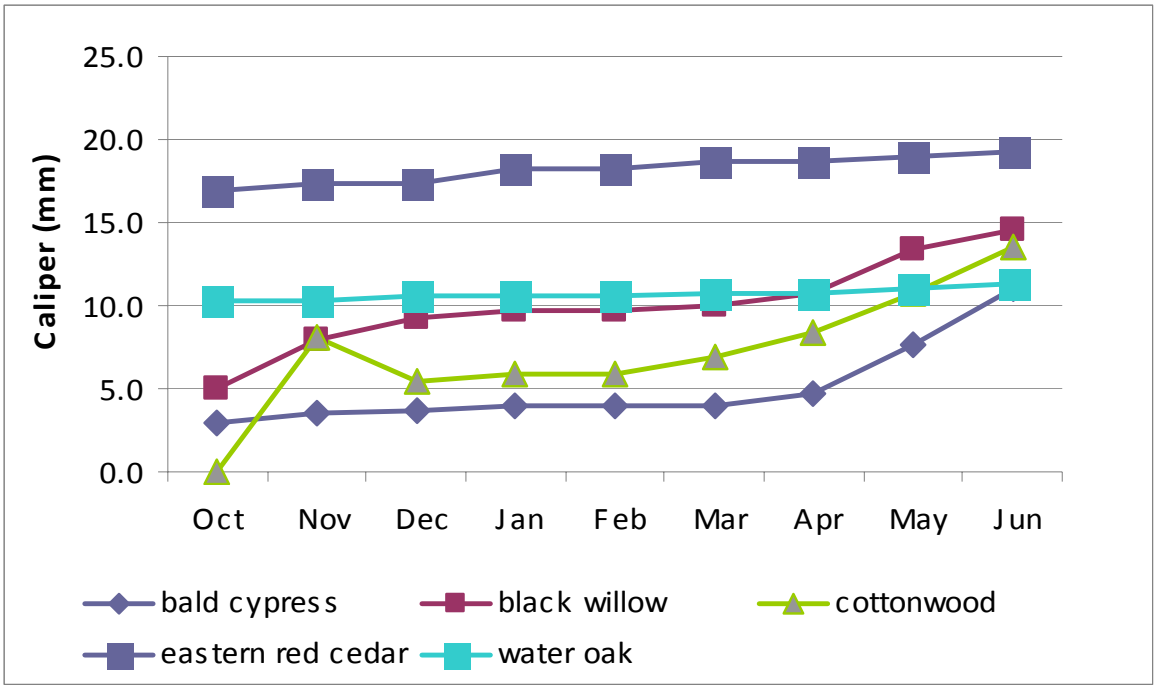

Figure 22. Average Caliper of Trees in the Water Use Experiment (mm)

Similar to height measurements, the caliper measurements of the eastern red cedar and water oak tree species did not vary considerable over the nine month study. The caliper measurements of bald cypress, black willow, and cottonwood trees noticbly began to increase in

April. All tree species had signifiacnt increases in caliper measurements between the months of October and June. Table 17 displays the mean caliper measurements.

Table 17. Average Caliper Diameter of Tree Species in the Water Usage Experiment

Species	October 2007 Caliper (mm)	June 2008 Caliper (mm)	Significance
Bald cypress	2.97	11.09	*
Black willow	5.02	14.62	*
Cottonwood	5.97	13.60	*
Eastern red cedar	16.87	19.26	*
Water oak	10.30	11.32	*

Values across rows with * are significant at $p \leq 0.05$.

All trees species calipers significantly increased between the months of October and June by ($p \leq 0.0001$) with the exception of the water oak trees which significantly increased by ($p \leq 0.05$). The eastern red cedars had the largest caliper diameters, followed by the black willow trees. However, note the increase in start to finish size of the black willows compared to the eastern red cedars. This quick increase in growth may be beneficial to the phytoremediation success as the black willows will quickly increase in size and potentially encounter the plume water faster than any of the other species. The June caliper measurements of the trees species were statistically compared against each other. The bald cypress trees had statistically smaller caliper sizes than cottonwood ($p \leq 0.03$), eastern red cedar ($p \leq 0.0001$), and black willow trees ($p \leq 0.001$). There was no significant difference in caliper size between the bald cypress and water oak species in the month of June. The black willow trees had significantly larger calipers than the water oak trees ($p \leq 0.003$). There were no significant differences between caliper sizes of black willow and cottonwood trees. But the eastern red cedar trees had statistically larger caliper measurements than the black willows. The cottonwood trees had statistically smaller caliper diameters than the eastern red cedars ($p \leq 0.0001$) but statistically larger caliper measurements than the water oaks ($p \leq 0.05$). The eastern red cedars had statistically larger caliper measurements than the water oaks ($p \leq 0.0001$).

Visual Rating

Figure 23 displays the mean monthly visual ratings for water usage trees. The averages and significances were determined by using a PROC Mixed SAS program accompanied by Saxton's Macro. Differences reported are Least Squares Means. Visual ratings rapidly began to decline in November. The ratings were lower because the trees naturally go dormant in the winter months. All trees with the exception of the eastern red cedar are deciduous. Even though the eastern red cedar is an evergreen, it still changes color in the winter months. The chlorophyll pigments break down and are masked by overwhelming amounts of xanthophylls and anthocynins. The eastern red cedars turn a purplish color in the winter. In March, all trees with the exception of the cottonwood trees began to return to their normal green color. The cottonwoods began turning green in April. The black willows and water oaks both declined in visual ratings between May and Jun. The black willow trees were using so much water that they completely dried out in between bi-weekly fillings twice during June.

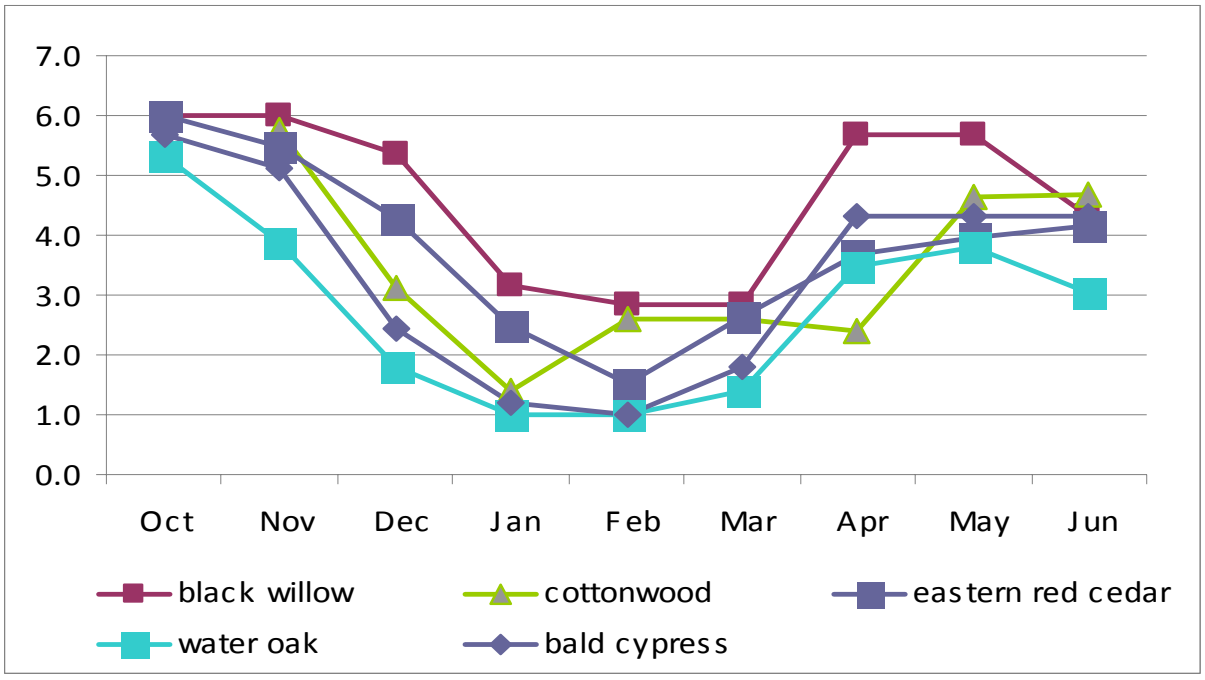

Figure 23. Average Visual Ratings of Trees in the Water Use Experiment

Therefore, the black willows dropped some leaves, thus making their visual rating scores lower in June. The water oak trees were not using much water so their decline in visual rating scores was not a result of drought. The best explanation for the decline in visual ratings of the water oaks between May and June is that their roots were becoming root bound. The same explanation is given for the lack of growth in the water oak species. Table 18 gives the average visual ratings of each species for the specific months of October and June.

All trees species visual ratings significantly declined ($p \leq 0.0001$) with the exception of the cottonwood trees between the months of June and October. The cottonwood tree visual ratings declined but not significantly. Only three of the fifteen cottonwood trees were given a visual rating score of 1.0 at the end of the study. Chemical treatments were not a part of this portion of the study. These values reflect changes in the individual species and are not attributed to any intentional variables. However, because the trees in this portion of the study were potted five to a trough, there were some troubles with drought, which caused leaf drop. After the first drought (no water remaining in trough at the end of the week) the troughs were filled bi-weekly. In the spring and summer months the black willows species continued to increase their water usage. Bi-weekly fillings were not sufficient. Therefore, the black willow troughs began receiving larger quantities of water at the start fill than the other tree species. The daily water liter usage reflects this increase. The drought periods did affect the visual ratings of the black willow tree species. In June, five of the fifteen black willows had a visual rating of 1.0. All ten other black willows had visual ratings of 6.0. If the trees with a rating of 1.0 were not included in the average then the average visual rating of black willows would be 6.0 and not significantly different from the start visual rating.

The bald cypress trees looked healthy in the water usage portion of the study. The decrease in visual ratings can be attributed to the lack of flushing out of leaves after the winter

month on some of the seedlings. The trees that did flush out were healthy species. Of the fifteen bald cypress trees five did not flush out and were given visual ratings of 1.0. However, all other ten bald cypress trees received a visual rating score of 6.0 in June. So, if the dead bald cypress were not counted in the final June average they would have had a visual score of 6.0 which would not have been significantly different than the starting rating.

Table 18. Average Visual Ratings of Tree Species in the Water Usage Experiment

Species	October 2007 Visual	June 2008 Visual	Significance
Bald cypress	5.67	4.33	***
Black willow	6.00	4.67	***
Cottonwood	5.19	4.67	NS
Eastern red cedar	6.00	4.17	***
Water oak	5.33	3.03	***

Values across rows with * are significantly different by p≤0.0001; NS = not significant.**

The eastern red cedar trees were healthy and receiving good visual ratings until the winter months. The trees did not return to their original dark green color. They went dormant and turned purple, and returned to a limey green color rather than the dark green color. This may be attributed to a lack of fertilizer or root binding. None of the eastern red cedars received a visual rating of 1.0 in June.

The water oak trees did not have sufficient time for full leaf emersion after the winter months. Like the eastern red cedars, none of the water oaks received visual rating scores of 6.0 in June.

Initial Tissue Samples

Target Compounds

No target compounds were identified in the initial tree samples. The lack of target samples in the initial tissue samples is reasonable as the COCs are not normally present in plant tissue.

Tentatively Identified Compounds

Both semi-volatile and volatile organic compounds were analyzed in the initial tissue samples. The tentatively identified compounds (TICs) can be possible metabolites of the parent compounds. However, no parent compounds (cumene nor 4-cumylphenol) were found in the root tissue of the three tree species. The initial TICs will be compared to the TICs in the final tissue samples. Those TICs that appear in both sets of samples can be disregarded, as they are most likely natural constituents of the root tissue. The initial TICs found in the plant tissue samples are listed in tables in the Appendix.

Final Tissue Samples

Target Compounds

The following target compounds were sampled for in the final tissue samples, Cumene, 4-cumylphenol, acetophenone, alpha, alpha DMBA, alpha methyl styrene, and phenol. Of these target compounds, cumene and 4-cumylphenol are the parent compounds, the rest are presumed metabolites as discussed in the introduction. The final target compounds table for COCs identified in the final tissue samples in the second greenhouse study is located in the Appendix (Table AB.3).

Four-cumylphenol was present in all three tree species in both the low and high water treatments. Cumene was not detected in any of the three species in any of the water treatments. Root tissue samples growing in the control water treatment were not intentionally spiked with chemicals. However, 4-cumylphenol was detected in the black willow control tissue samples. All 4-cumylphenol found in control black willow samples were detected at J values, meaning that the reported value was an estimated concentration above the instrument's method detection limit and below the laboratory reporting limit. If this trace amount of 4-cumylphenol really did exist in the black willow control tissue samples, then there are two possible methodology explanations.

Trace levels of chemical might have carried over from the troughs from year one to year two. Precaution was taken to make sure that DI water troughs in year 2 were the same as DI water troughs in year 1. The other possible explanation is chemical contamination may have been caused by backflow during draining. Each time the troughs were drained, they were drained one water treatment at a time. All troughs had to be drained before opening the drainage valves on another set of troughs that held a different water treatment because the water would back flow into any open troughs. Residual water in the main pipe (PVC) pipe might have back flowed into the DI troughs causing a small but traceable amount of chemical contamination. There was no indication of the samples being mislabeled.

The black willows retained the highest levels of 4-cumylphenol of the tested tree species in both low and high water treatments. The average concentration of 4-cumylphenol in black willow roots was 16.6mg/kg for the low treatment and 21.4mg/kg in the high water treatment. The average concentration of 4-cumylphenol in bald cypress roots was 1.7mg/kg for the low treatment and 1.5mg/kg in the high water treatment. The average concentration of 4-cumylphenol in cottonwood roots was 1.5mg/kg for the low treatment and 3.8mg/kg in the high water treatment.

Both the black willow and cottonwood tissue samples from the high water treatment had detectable levels of α, α- DMBA. As discussed in the introduction, α, α- DMBA is a possible metabolite of cumene.

Tentatively Identified Compounds

Both semi-volatile and volatile organic compounds were analyzed in the final tissue samples. The tentatively identified compounds (TICs) are possible metabolites of the parent compounds. Since the parent compound 4-cumylphenol was found in the final root tissue samples of all three-tree species, the initial TICs were compared to the final TIC results. TICs

that appeared in both sets of samples were disregarded because they are most likely natural constituents of the root tissue. TICs that appeared in the final root samples of the tree tissue growing in low and high water treatments were also compared to final TICs found in tree root tissue growing in the DI water treatment. If the same TIC appeared in both the contaminated and non-contaminated water samples it was disregarded because no chemicals were intentionally spiked in the DI water treatment. Several TICs were found in the final root samples that were not found in the initial root samples or in the final DI water root tissue samples. The TICs are divided into VOCs and SVOCs. The VOC and SVOC initial and final TIC tables are located in the Appendix.

The following listed TIC compounds met two criteria. The first is that the TICs were detected in high or low water treatment trees but not the control water treatment trees. The second criterion was that the TIC was detected only in the final root tissue samples and not in the initial root tissue samples.

In the low water treatment black willow root samples two VOC TIC's were identified, pentane (C_5H_{12}) 0.03mg/kg and 1-octen-3-ol ($C_8H_{16}O$) 0.21mg/kg.

Only one VOC TIC was identified in the final high water treatment black willow root sample, α - pinene ($C_{10}H_{16}$) 0.027mg/kg . It should be noted that in the first year greenhouse phytotoxicity study, α – pinene ($C_{10}H_{16}$) was found in non-contaminated tissue samples.

Two VOC TICs were identified in the final low water treatment cottonwood root samples; they were acetone (C_3H_6O) 0.07mg/kg and 1- octen-3-ol ($C_8H_{16}O$) 0.34mg/kg.

Two VOC TICs were identified in the high water treatment bald cypress root samples; they were α – pinene ($C_{10}H_{16}$) 0.08mg/kg and 1, 4- pentadiene, 2, 3, 3- trimethyl- (C_8H_{14}) 0.02mg/kg.

There were no new VOC TICs in the high water treatment cottonwoods or low water treatment bald cypress trees.

The VOC TICs that were identified did not equal the mass of contaminants that went into the hydroponic system. For example, there was 0.21mg/kg of 1-octen-3-ol in the III 50 1 black willow tissue sample. The root mass of that particular sample was 982grams. Approximately 899.7mg of 4-cumylphenol and 210.5 mg of cumene were added to Block III of the hydroponic system throughout the study. Therefore the TIC amounted to less than 1% of the total mass of parent compound introduced to the hydroponic system. This indicates that this TIC and other VOC TIC's were not significant metabolites of the parent compounds.

A few SVOC TICs were identified in the final root tissue samples that were not identified in the initial root tissue samples or in the final DI water samples. Of these, several were disregarded because their molecular weights were greater than 4-cumylphenol and they had more complex structures than the original parent compounds.

The SVOC TIC's that were identified are listed below. The SVOC TIC's listed have met the same two criteria that the VOC TIC's met. They were not identified in the DI or control tissue samples and they were not identified in the initial tissue samples.

Vanillin, (synonym is 4-hydroxy –3-methoxy – benzaldehyde) ($C_8H_8O_3$) 0.8mg/kg was identified in a low water treatment bald cypress root sample. Vanillin is common in plant–based food materials and could be a natural component of plants.

Two- Propenoic acid, 3-phenyl- ($C_9H_8O_2$) 1.5 and 1.1mg/kg was identified in two of the cottonwood samples in the low water treatment and one of the cottonwood root samples in the high water treatment 1.3mg/kg. 9H –Xanthene ($C_{13}H_{10}O$) 2.1mg/kg was identified in one cottonwood root sample from the high water treatment.

Vanillin (Benzaldehyde, 4-hydroxy –3-methoxy) (C8H80) 0.8mg/kg was identified in a bald cypress root in the high water treatment.

The final SVOC TIC identified was 2-cyclohexen-1-one (C6H8O) 11mg/kg identified in a black willow root from the high water treatment.

Again, the SVOCs similar to the VOCs amounted to less than 1% of the total mass of parent compound that was added to the hydroponic system, and are not considered to be significant metabolites of the parent compounds.

Initial Media Samples

Four composite media samples were taken at the time of media preparation. The purpose of initial media sampling was to analyze for the presence of cumene and 4-cumylphenol prior to the start of the study. If, cumene or 4-cumplyphenol were found in the initial media samples, then that amount would be subtracted from the total mass of COC's introduced during the system. Table 19 displays the surrogate corrected concentrations of cumene and 4-cumylphenol in the initial media samples.

Table 19. Cumene and 4-Cumylphenol in Initial Soil Samples

Chemical	**I Soil 1**	**I Soil 2**	**I Soil 3**	**I Soil 4**
	Conc. (ng/mg)	**Conc. (ng/mg)**	**Conc. (ng/mg)**	**Conc. (ng/mg)**
Cumene	0.00	0.00	0.00	0.00
4-Cumylphenol	0.03	0.03	0.03	0.02
Surrogate Recovery	1.0	0.99	1.2	0.99
Surrogate Corrected	**Conc. (ng/mg)**	**Conc. (ng/mg)**	**Conc. (ng/mg)**	**Conc. (ng/mg)**
Cumene	0.00	0.00	0.00	0.00
4-Cumylphenol	0.03	0.03	0.02	0.02

Cumene was not present in the media prior to the start of the study. 4-Cumylphenol was detected in the soil prior to the start of the study. However, the trace concentrations of 4-cumylphenol were detected at a detection rate below the reporting limit used at PACE Analytical Lab. The PACE reporting limit for 4-cumylphenol in soil is 0.33mg/kg. Therefore, the amount of 4-cumylphenol detected by LSU in the initial soil samples can be considered as a J value or

below what is typically reported by PACE Analytical Lab. The LSU Toxicology lab has a practice of using the surrogate corrected values for soil reports.

Final Media Samples

Soil samples were taken at the end of the greenhouse study. The final soil samples were collected to account for a portion of the mass of chemicals introduced to the hydroponic system. Tables 20-22 display the final concentrations of chemicals in the media.

Soil sampled from the DI pots contained trace concentrations of cumene and 4-cumylphenol below typical PACE Analytical Lab reporting limits. Two of the soil samples that originally contained bald cypress trees had trace amounts of the parent compounds. All four soil samples that held cottonwood trees had trace amounts of 4-cumylphenol below reliable detection limits. No cumene was detected in soil samples that orginially held cottonwood trees. Two of the four DI soil samples originally containing black willow trees had concentrations of cumene below detectable concentrations. 4-Cumylphenol was not detected in any of the DI soil samples containing black willow trees. There is no TIC data for media in the seond year of study.

Sludge Samples

Sludge samples were taken after the greenhouse study was complete. Sludge can be defined as the remaining soil and debris and water in the troughs after complete drainage. There was little sludge in the second greenhouse study when compared to the first greenhouse study. The lack of sediments and debris can be attributed to using DI water in year two compared to using well water in year one. Because of the lack of sediment and debris, liquid to liquid extractions were completed to analyze the sludge samples in year two. Tables 23-25 display the final data for sludge samples.

Table 20. Cumene and 4-Cumylphenol in Final Soil Samples DI Treatment

Sample Description	I DI 3 BC SOIL	III DI 3 CW SOIL	I DI 3 BW SOIL	II DI 2 BC SOIL	II DI 2 CW SOIL	I DI 2 BW SOIL	II DI 1 BW SOIL	III DI 1 BC SOIL	III DI 2 BC SOIL	III DI 1 CW SOIL	I DI 3 CW SOIL	II DI 2 BW SOIL
	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg
Cumene	0.00	0.00	0.07	0.52	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00
4-Cumyl-phenol	0.01	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Surrogate Recovery	1.1	1.2	1.1	0.87	1.1	0.80	0.94	0.91	1.00	1.2	0.67	1.02
Surrogate Corrected	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg
Cumene	0.00	0.00	0.06	0.60	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00
4-Cumyl-phenol	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.02	0.00

DI = deionized water. BC = bald cypress, CW = cottonwood, BW= black willow

Table 21. Cumene and 4-Cumylphenol in Final Soil Samples Low Treatment

Sample Description	I 50 2 BC SOIL	II 50 3 BC SOIL	III 50 3 BC SOIL	I 50 1 BW SOIL	II 50 1 BW SOIL	III 50 1 BW SOIL	III 50 3 BW SOIL	I 50 1 CW SOIL	II 50 1 CW SOIL	II 50 3 CW SOIL	III 50 3 CW SOIL	III 50 1 BC SOIL
	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg
Cumene	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Cumyl-phenol	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01
Surrogate Recovery	1.2	0.94	0.97	1.10	0.91	0.81	0.86	1.10	1.00	0.84	1.02	1.14
Surrogate Corrected	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg
Cumene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Cumyl-phenol	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01

50 = low water treatment. BC = bald cypress, CW = cottonwood, BW= black willow

Table 22. Cumene and 4-Cumylphenol in Final Soil Samples High Treatment

Sample Description	I 100 1 BC SOIL	I 100 2 BC SOIL	II 100 2 BC SOIL	III 100 1 BC SOIL	I 100 2 CW SOIL	I 100 3 CW SOIL	II 100 2 CW SOIL	III 100 2 CW SOIL	I 100 3 BW SOIL	III 100 2 BW SOIL	III 100 1 BW SOIL	I 100 2 BW SOIL
	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. (ng/mg)	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg
Cumene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Cumyl-phenol	0.01	0.00	0.00	0.02	0.01	0.00	0.00	0.04	0.00	0.00	0.01	0.01
Surrogate Recovery	0.95	0.86	0.95	1.04	1.15	1.15	1.19	0.98	1.20	1.19	1.20	1.10
Surrogate Corrected	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg	Conc. ng/mg
Cumene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Cumyl-phenol	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.04	0.00	0.00	0.01	0.01

100 = high water treatment. BC = bald cypress, CW = cottonwood, BW= black willow

Table 23. Cumene and 4-Cumylphenol in Final DI Sludge Samples

Sludge treatment	I DI 1 sludge	I DI 2 sludge	I DI 3 sludge	II DI 1 sludge	II DI 2 sludge	III DI 1 sludge	III DI 2 sludge	III DI 3 sludge
	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Cumylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Surrogate Recovery	1.17	1.14	1.17	1.01	1.17	1.09	1.18	1.20
Surrogate Corrected	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Cumylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 24. Cumene and 4-Cumylphenol in Final Low Treatment Sludge Samples

Sludge Treatment	I 50 1 SLUDGE	I 50 2 SLUDGE	II 50 1 SLUDGE	III 50 1 SLUDGE	III 50 2 SLUDGE
	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	0.46	2.14	0.35	0.36	0.51
4-Cumylphenol	0.00	0.00	0.00	0.00	0.00
Surrogate Recovery	1.13	0.17	1.08	1.13	1.20
Surrogate Corrected	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	0.403	12.698	2.107	0.314	0.470
4-Cumylphenol	0.000	0.000	0.000	0.000	0.000

Table 25. Cumene and 4-Cumylphenol in Final High Treatment Sludge Samples

Sludge Treatment	I 100 1 SLUDGE	I 100 2 SLUDGE	I 100 3 SLUDGE	II 100 1 SLUDGE	II 100 2 SLUDGE	III 100 1 SLUDGE	III 100 2 SLUDGE
	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	1.78	0.06	0.18	0.82	0.00	0.17	0.57
4-Cumylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Surrogate Recovery	1.18	1.04	1.20	1.20	0.95	1.02	0.85
Surrogate Corrected	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	1.509	0.057	0.150	0.687	0.000	0.168	0.669
4-Cumylphenol	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Cumene and 4-cumylphenol were not found in the DI sludge samples. This was expected, as these chemicals were not intentionally introduced into the DI hydroponic troughs. The low water treatment troughs contained levels of anywhere from 0.4 to 2.0μg/mL cumene. The parent compound, 4-cumylphenol was not detected in the low water treatment troughs. The high water treatments contained anywhere from approximately 0.00 to 1.50μg/mL cumene. Like the low water treatment troughs, 4-cumylphenol was not detected in the sludge samples. The total mass of cumene found in the sludge samples is less than 0.5% of the total mass of cumene added to the hydroponic system.

Final Nutrition Samples

Tables 26-31 compare mineral concentrations of DI, Low, and High water treatments for each tree species.

There were no significant differences in mineral concentrations for the bald cypress roots growing in any of the water treatments. The bald cypress tops growing in the high water treatment were significantly higher ($p \leq 0.05$) in concentrations of both Ca and Zn than those bald cypress tops growing in the low and DI water treatments. Ca sufficiency concentrations reported by Mills et al., 1996, are 1.37-1.98% the bald cypress tops fell below this range. The low water treatment mean concentration of Zn was much higher than reported concentrations (22μg/mL) of Zn in bald cypress tissue (Mills et al., 1996). Boron concentrations ranged from significantly highest in the low water treatment followed by the high water treatment and then DI water treatment ($p \leq 0.005$). Only the B concentrations in the DI water treatment were well below the reported concentration of 48mg/kg B in bald cypress tissue (Mills et al., 1996).

Table 26. Mean Nutrition Values of Bald Cypress Root Samples

Water Trt	P	K	Ca	Mg	Na	Fe	Zn	Mn	S	Cu	B
DI	0.20[Z]	0.87	0.38	0.36	0.09	4616.75	71.63	528.25	0.24	32.83	17.40
Low	0.17	0.81	0.44	0.43	0.12	6440.25	75.48	640.75	0.25	42.15	23.88
High	0.18	0.77	0.59	0.55	0.10	4384.00	241.20	388.00	0.30	41.28	42.48
Significance	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

[Z] Means within columns with different letters are significantly different. NS= not significant. Means obtained using a PROC GLM SAS program and Duncan. Low= 0.50µg/mL cumene + 2µg/mL 4-cumylphenol, High= 1µg/mL cumene + 4µg/mL 4-cumylphenol.

Table 27. Mean Nutrition Values of Bald Cypress Top Samples

Water Trt	P	K	Ca	Mg	Na	Fe	Zn	Mn	S	Cu	B
DI	0.13	0.90	0.31B	0.21	0.06	129.00	30.95B	66.00	0.13	7.75	18.95C
Low	0.17	0.92	0.37B	0.24	0.06	198.50	605.30B	83.78	0.15	11.21	43.15A
High	0.17	1.19	0.58A	0.34	0.19	462.50	37.13A	102.18	0.19	15.83	30.13B
Significance	NS	NS	*	NS	NS	NS	*	NS	NS	NS	*

[Z] Means within columns with different letters are significantly different * = p≤0.05; NS= not significant. Means were obtained by using a PROC GLM SAS program and Duncan. Low= 0.5µg/mL cumene + 2µg/mL 4-cumylphenol, High= 1µg/mL cumene + 4µg/mL 4-cumylphenol.

Table 28. Mean Nutrition Values of Black Willow Root Samples

Water Trt	P	K	Ca	Mg	Na	Fe	Zn	Mn	S	Cu	B
DI	0.21	1.05	0.29	0.25	0.11	1430.50	121.65	343.50	0.25	16.88	24.75
Low	0.18	0.75	0.31	0.19	0.07	1367.25	90.48	341.50	0.19	13.40	16.48
High	0.21	0.80	0.30	0.18	0.07	611.75	87.43	192.50	0.18	13.80	16.78
Significance	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

[Z] Means within columns with different letters are significantly different NS= not significant. Means were obtained by using a PROC GLM SAS program and a Duncan. Low= 0.5µg/mL cumene + 2µg/mL 4-cumylphenol, High= 1µg/mL cumene + 4µg/mL 4-cumylphenol.

Table 29. Mean Nutrition Values of Black Willow Top Samples

Water Trt	P	K	Ca	Mg	Na	Fe	Zn	Mn	S	Cu	B
DI	0.19	0.91	0.40	0.22	0.02	172.25AB	71.65	184.25	0.20	9.08	19.03
Low	0.17	0.81	0.40	0.17	0.02	124.08B	64.90	202.00	0.18	9.14	16.00
High	0.20	0.79	0.45	0.21	0.01	361.50A	84.40	203.25	0.18	10.96	16.58
Significance	NS	NS	NS	NS	NS	*	NS	NS	NS	NS	NS

[Z] Means within columns with different letters are significantly different * = p≤0.05; NS= not significant. Means were obtained by using a PROC GLM SAS program and a Duncan. Low = 0.5µg/mL cumene + 2µg/mL 4-cumylphenol, High = 1µg/mL cumene + 4µg/mL 4-cumylphenol.

Table 30. Mean Nutrition Values of Cottonwood Root Samples

Water Trt	P	K	Ca	Mg	Na	Fe	Zn	Mn	S	Cu	B
DI	0.18	0.58	0.57	0.40	0.14	29976.75	3361.25A	440.50	0.23	22.60	32.05
Low	0.23	0.71	0.51	0.36	0.07	3605.75	750.00B	422.00	0.24	26.53	20.28
High	0.20	0.66	0.63	0.46	0.11	3863.25	1143.75B	473.75	0.25	25.09	23.18
Significance	NS	NS	NS	NS	NS	NS	*	NS	NS	NS	NS

[Z] Means within columns with different letters are significantly different *= p≤0.05; NS= not significant. Means were obtained by using a PROC GLM SAS program and a Duncan. Low = 0.5µg/mL cumene + 2µg/mL 4-cumylphenol, High = 1µg/mL cumene + 4µg/mL 4-cumylphenol.

Table 31. Mean Nutrition Values of Cottonwood Top Samples

Water Trt	P	K	Ca	Mg	Na	Fe	Zn	Mn	S	Cu	B
DI	0.21	1.27	0.85	0.47	0.19	315.00	2331.33	161.27	0.30	7.70	55.60
Low	0.27	0.87	0.52	0.42	0.07	203.55	281.50	226.50	0.22	7.04	33.98
High	0.31	1.11	0.92	0.59	0.10	367.25	931.25	367.25	0.38	6.17	33.83
Significance	NS	NS	NS	NS	NS	NS	NS	*	NS	NS	NS

[Z] Means within columns with different letters are significantly different * = p≤0.05; NS= not significant. Means were obtained by using a PROC GLM SAS program and a Duncan. Low = 0.5µg/mL cumene + 2µg/mL 4-cumylphenol, High = 1µg/mL cumene + 4µg/mL 4-cumylphenol.

There were no significant differences in mineral concentrations for the black willow roots growing in any of the water treatments. The only significant difference in mineral concentration for the black willow tops was Fe. There was a significant difference ($p \leq 0.09$) between the Fe concentrations of those black willows growing in the high water treatment compared to the Low water treatment. Neither of the contaminated water treatments differed from the DI water treatment. The high water treatment mean concentrations of Fe in black willow tops were above the reported concentration of 132mg/kg, whereas, the DI and low treatments were much closer to reported concentrations (Mills et al., 1996).

There were no significant differences in concentrations of any minerals in the cottonwood root samples with the exception of Zn. The Zn concentration was significantly higher in the DI water treatment than both the low and high water treatments ($p \leq 0.05$).Zn concentrations in the DI, low and high water treatments were above the reported value of 199mg/kg concentration in cottonwood tissue (Mills et al., 1996). There were also no significant differences in mineral concentration within the cottonwood tops growing in all water treatments with the exception of Mn. The Mn concentration was significantly greater in the High followed by Low and then DI water treatments ($p \leq 0.05$). The Mn concentration of the cottonwood tops growing in all three water treatments were above the reported concentration (106mg/kg Mn), however they weren't too much higher (Mills et al., 1996).

Based on all findings of nutrition levels, the trees did not seriously suffer from any nutritional deficiencies throughout the experiment. In most cases the mineral levels were within reported values or slightly higher. However, the visual ratings of the three tree species throughout the study did not indicate nutrient deficiencies or toxicity.

CHAPTER 6

CONCLUSIONS

GREENHOUSE PILOT STUDIES CONCLUSIONS

First Year Pilot Study

Based on the phytotoxicity pilot study the bald cypress is the optimum tree species for full scale planting over the Stratum III groundwater plume. The bald cypress trees were the most tolerant species to the salinity treatments. The bald cypress was also able to significantly increase in caliper diameter and height measurements over the course of the study when subjected to the COC's. Since the bald cypress is a conical formed tree remaining narrow, it is an ideal tree for close spacing, which is necessary to achieve the best root coverage to remediate the contaminated area. It can also be pruned into a hedge, (Gilman and Watson, 1994) which makes this species practicable because of Georgia Gulf's security precautions in this area of the site. A monoculture of bald cypress should not be a problem since there is no known insect or diseases that affect bald cypress in south Louisiana.

Second Year Pilot Study

The final data indicates that the bald cypress and black willow species have phytoremediation capabilities and acceptable plant quality after exposure to cumene and 4-cumylphenol spiked water.

Plant quality was measured using a combination of height and caliper measurements and visual ratings. Of the trees subjected to chemically treated water, the tallest tree (in June) was the black willow with average heights of 3.8 – 4.1m followed by the cottonwood and bald cypress with average heights of 1.0-1.2m and 1.0m respectively. The tree with the largest caliper was the black willow with average caliper measurements of 22.0mm followed by the cottonwood and bald cypress with average caliper measurements (in all water treatments) of 12.0-14.0mm and 13.0mm respectively. The bald cypress caliper and height measurements in the low and high

water treatments were not significantly different from caliper and height measurements of bald cypress growing in the DI water.

The average visual rating of bald cypress trees in the high water treatment was low at the end of the study. However, the purpose of the high water treatment was to test the trees tolerance at the highest recorded water contamination rate. In a field situation, the trees would not be exposed to these high levels of contamination because trees draw a majority of water from their feeder roots. The feeder roots are those roots within the first 0.61-0.91m below the ground surface. Therefore, the tree roots will translocate diluted plume water. Visual results indicated that the black willow tree was the only tree with a 6.0 visual ratings at the end of the study. The cottonwood and bald cypress trees maintained 4 - 4.5 and 4 - 5.8 visual ratings respectively at the end of the study. Of the trees that survived, the visual ratings were above average. Those trees that died may have done so because of small starting size as seedlings. It is not uncommon in the horticulture industry to lose a large percent of nursery crop that start as seedlings.

In addition to plant quality the concentrations of COCs and TICs detected in final plant tissue was an important factor in selecting the tree species for full-scale implementation of phytoremediation at the closed and capped impoundment area. Four-cumylphenol was detected in the roots (growing in low and high water treatments) of all three tree species. The black willow had the highest concentrations of 4-cumylphenol detected. This probably occurred because of the size and amount of water that the black willow took up compared to the cottonwood and bald cypress species. There were no significant TICs found in the tree tissue.

The back portion of the greenhouse was dedicated to the water usage experiment. When trees were grown in DI water alone, the trees utilizing the largest quantities of water were the black willow, followed by the cottonwood, then bald cypress trees. Naturally, the black willows and cottonwood trees used more water than the bald cypress because they were larger species.

Water usage continued throughout the winter months for all tree species. This is important because ideally hydraulic control of the plume would be maintained year round.

The factors above plus several others have lead to the conclusion that the bald cypress species may be best suited for phytoremediation at the closed and capped surface impoundment located at Georgia Gulf facilities. The following bullets provide support that the bald cypress species is well suited for full scale planting.

- COC Tolerance. The bald cypress tree was tolerant of the chemicals in the water at the low and high water treatments. As noted before, the high water treatment was used in the study to attempt to determine a critical point. The trees when planted in the field will not be exposed to concentrations of chemicals as high as those in the high water treatment.
- Salinity Tolerance. In the Phase I study (year 1), the bald cypress tree was the only species that was tolerant of the 100% salt-water treatment. The 100% salt water treatment during the Phase I study was representative of the relatively high salinity (above 2.0mS) that is present in the groundwater plume. This treatment water contained minimal or no concentrations of cumene and 4-cumylphenol, so as to identify the effects of salinity on candidate tree species
- Root Growth. Although the black willow species was the largest as far as height and caliper, and utilized the most water, its roots do not penetrate as deeply into the ground as the bald cypress roots will. This is an important factor as the ground water plume is located ten to twenty-two feet below ground surface. If rainfall is plenty, which is likely in south Louisiana, then the black willow roots will grow more laterally compared to the bald cypress. Even in a drought period the black willow is not likely to reach the lower portions of the plume where the chemical concentrations are present.

- Resistance to Wind Damage. After Hurricane Gustov, it was noticeable that black willows in the Plaquemine and Baton Rouge areas had sustained greater damage than bald cypress trees. Bald cypresses appear to be less likely to topple over and lose a considerably less amount of branches and leaves than the black willow.
- Maintenance. Black willows naturally create considerable litter. A tree that requires minimal maintenance is a priority. A clear path is need between tree rows for mowing. Loose debris is also not desirable in case of high winds. Tree form also plays a role in maintenance and security. The black willow has a sprawling form whereas the bald cypress is conical shaped. The black willows grow at rapid rates, which would lead to increased effort to prune and maintain the shape and form of the tree for security purposes. Bald cypress trees can be hedged which will provide clearance for security camera angles if needed. Security cameras require a clear view along the perimeter fence line where the trees will be planted. The bald cypress tree would require much less maintenance than the black willow and cottonwood species.

While the black willow tree species would be acceptable trees for phytoremediation of the contaminants, the bald cypress tree is effective for phytoremediation and is the tree species that is most compatible with Georgia Gulf security requirements.

Full Scale Planting

Before the full scale planting began, the entire area covering the closed and capped impoundment groundwater plume was tilled. Following tillage, approximately 1 ton of gypsum per acre will was applied to the area. Soil test results from this area were high in salts. The gypsum application should leach the salts and improve soil tillage. After the gypsum was applied, holes for the trees will be dug. The safety factor calculation for hole heave allowed the holes to be dug approximately 4 feet in depth with an assumed safety factor (SF) of 1.5. This

depth limitation will not allow any of the groundwater to rise into the planting hole but will break up any existing hard pan allowing tree roots to penetrate faster into the groundwater plume. The calculation for the safety factor of soil heave is shown below. A maximum confined head of 8 feet was assumed.

(soil thickness beneath hole) * (soil density) = SF * (water head) * (water density)

X * (120lbs/ ft3) = (1.5) (8ft) (63ilb/ft3)

X = 6.3 ft

Hole depth = 10-6.3 = 3.7ft

The holes were dug with an agar implementation on a backhoe. The original soil removed from the holes was used to backfill the holes. The holes were left unplanted for several days. This time period allowed the backfilled soil to settle in the holes. Planting the trees immediately would have caused the trees to sink. Even with the several day period of rest, several trees sank after the planting. Those trees had to be removed from the holes, soil added, and the trees replanted.

Cypress trees were planted in two staggered rows of twenty-four trees each, placed on eight to ten foot center spacing depending on well location. The trees were placed in the original holes so that the root ball was level with the ground surface. Three gallon bald cypress trees were planted.

An irrigation system was designed and built to water trees during dry periods. The irrigation system will remain in place until the first summer has past. The irrigation system was designed to deliver water at a rate of 2 acre-inches per week when precipitation is insufficient. An acre-inch is approximately 27,154 gallons of water (Davidson *et al.*, 2000). The irrigation system connects to the potable water source located on the clarifiers near the full scale planting

area. Poly pipe was buried along each row of trees. A riser and emitter were placed at the base of each tree.

PSI employees will monitor the trees for insect, disease, drought symptoms, and canopy control until well established.

CHAPTER 7

CUMENE AND 4-CUMYLPHENOL TOXICITY STUDY

BACKGROUND

Greenhouse trials were conducted to determine a young tree's (approximately 1 year) survivability and potential phytoremediation of cumene and 4-cumylphenol contaminated water. Additional evaluations were conducted to determine the toxicity of cumene and 4-cumylphenol on seed germination and radical length. The primary objective of the second study was to determine if cumene and 4-cumylphenol are toxic to plants. In order for phytoremediation to be an acceptable method for remediation of contaminated groundwater, the COCs must not be toxic to plants. There is relatively no published information on toxic levels of cumene and 4-cumylphenol on plant material.

To determine toxicity, a Phytotoxkit™ including three plant species *Sorghum saccharatum*, *Lepidium sativum*, and *Sinapis alba,* was used. The seeds included in the Phytotoxkit™ were chosen for their rapid germination rates under normal conditions. It is not uncommon to use edible plants as pollution remediators. Cobbett and Meagher (2002) reviewed studies that looked at *Arabidopsis* (Mustard family) as a potential plant species for phytoremediation of heavy metals and organic pollutants. Schnabel and colleagues (1997) studied the ability of carrots, spinach, and tomatoes to remediate trichloroethylene contaminated water.

INTRODUCTION

A groundwater plume is contaminated with two volatile and semi-volatile organic chemicals, cumene and 4-cumylphenol. Cumene causes increased kidney weights in rats (Foureman, G.L., 1997). Four-cumylphenol is a suspected endocrine disruptor (Tan *et al.*, 2007). Both contaminants are present in higher concentrations than LADEQ allows. A greenhouse study was conducted to determine if phytoremediation is a feasible remediation method for removal of the contaminants. However, there is little information on the potential toxicity of these chemicals

to plants. Therefore, this laboratory experiment was conducted to determine if the contaminated plume water would effect germination and radical length of higher order plant seeds. Based on findings from the initial study, a second lab study was conducted to determine effects of contaminates at higher concentrations than the plume water. Both experiments were conducted using a Phytotoxkit™. Results of the experiments will contribute information on the potential plant toxicity of cumene and 4-cumylphenol.

MATERIALS AND METHODS

Two experiments were conducted at different levels of water contamination. Seeds of three plant species (*Sorghum saccharatum, Lepidium sativum, and Sinapis alba*) were evaluated. Water treatments included a control (DI water) and contaminated (1.7µg/mL cumene & 4µg/mL 4-cumylphenol) water in the first experiment. Water treatments in the second experiment were control (DI water), contaminated 1 (25µg/mL cumene & 4-cumylphenol), and contaminated 2 (50µg/mL cumene & 4-cumylphenol). Both experiments were conducted using the following procedure.

Soil was sieved through a 1.4mm sieve. 90.0mL's of soil was placed in each tray. Trays were provided in the Phytotoxkit™. Then 42.0mL's (WHC) of water was added to the soil. Saturated soil was spread evenly in the lower compartment of the tray. Ten seeds were placed in a horizontal line on top of filter paper lining the lower compartment of each tray (one species per tray). The trays were then sealed with a clear cover and placed in an incubator at 25ºC for 4d (6d for the second experiment). Light was not used for germination. After incubation, digital images of each tray were taken. Root lengths were measured using UTHSCSA Image Tools version 3.00©. Data was analyzed using a PROC Mixed SAS program. The number of germinated seeds was counted in each tray. Percent germination inhibition was calculated using the equation; (A-B) / A * 100 = % germination inhibition. A = the total number of germinated seeds in the control

water. B = the total number of germinated seeds in the contaminated water. For each experiment, six trays per seed type and three trays per water treatment were used. The entire experiment was replicated twice.

RESULTS

First Experiment

Root Length

Average root length of seeds sprouted in control water (46.85mm) was significantly different than average root lengths of seeds sprouted in contaminated water (52.49mm) for all species combined ($p \leq 0.0405$). *Lepidium* root lengths were significantly longer when grown in contaminated water compared to deionized water ($p \leq 0.0322$). There were no significant root length differences in either *Sinapsis* or *Sorghum* seeds grown in deionized or contaminated water.

Table 32. Mean Root Length of Germinated Seeds (mm)

Species	Mean root length (mm) Contaminated water	Mean root length (mm) DI water	Significance
Lepidium	55.17 A	45.13 B	*
Sinapsis	57.70 A	52.33 A	N.S.
Sorghum	44.57 A	43.54 A	N.S.

Values across rows with different letters are statistically significant at p≤0.0322.

Germination Percentages

The contaminated water did not affect germination of *Lepidium* and *Sinapsis* seeds. There was 100% germination of both species of seeds in the deionized and contaminated water. However, there was significantly greater germination of *Sorghum* seeds in the contaminated water verses the deionized water ($p \leq 0.0001$). Twenty-nine of the 30 contaminated seeds germinated while only 26 of the 30 deionized water seeds germinated. These results indicate that at this level of contamination (1.7µg/mL cumene 4µg/mL 4-cumylphenol) germination was not negatively affected.

Second Experiment

Root Length

There were no significant differences in root length between seeds sprouted in 0, 25, or 50μg/mL contamination treatments for any of the individual species. However, there was a significant difference between species ($p \leq 0.0001$). *Lepidium* roots were longer than both *Sinapsis* and *Sorghum* roots in all water treatments, indicating a difference in species. These findings indicate that chemical contamination at 25 and 50μg/mL has no significant effect on radical length.

Germination Percentages

There were no significant differences in seed germination percentage in any of the three plant species. There was no significant inhibition of germination caused by cumene or4-cumylphenol in the three tested species. Therefore, these contaminants do not have an effect on germination of the three species.

CONCLUSIONS

Sorghum seeds had a significantly higher germination rate in the contaminated water (1.7μg/mL cumene and 4μg/mL 4-cumylphenol) than the deionized water in experiment one. In experiment two, cumene and 4-cumylphenol (contaminated water) did not have any effect on seed germination. An increase in mean root length of *Lepidium* roots occurred in contaminated water (1.7μg/mL cumene + 4μg/mL 4-cumylphenol) in experiment one. There was no significant difference in root lengths detected in the second experiment. This would indicate that this effect is rate dependent. At lower levels of contamination, the chemicals at hand may act as a stimulus for seed germination. This research establishes the first baseline data on seed and plant growth for cumene and 4-cumylphenol.

CHAPTER 8

FATE AND TRANSLOCATION PHYTOTOXICITY STUDY

INTRODUCTION

The third experiment of the dissertation project was initiated to determine the fate of cumene and 4-cumylphenol within *Salix nigra's* tissue. The purpose of the additional lab study was to ascertain translocation and fate of cumene and 4-cumylphenol when introduced hydroponically to a rooted cutting. Results from the greenhouse experiments determined that bald cypress trees were the best match for phytoremediation of the groundwater plume at the closed and capped impoundment area in Plaquemine, Louisiana. However, the presence of cumene and 4-cumylphenol was substantial on final root samples of some of the black willow species in the first greenhouse experiment. The total mass of inputted chemical was not accounted for in the total concentrations of cumene and 4-cumylphenol on the black willow roots. Therefore, documenting the movement of cumene and 4-cumylphenol and their metabolites in a lab setting would offer a more determinate conclusion as to the fate of the chemicals once introduced into the system.

Several studies (McFarlane et al., 1990; Trapp et al., 1990; Wang and Jones, 1994; Paterson et al., 1994; and Chang and Corapcioglu, 1998) have used similar experiments to access the fate of organic contaminants in plants. Corseuil and Moreno (2001) found that lab scale studies indicated that willow species may significantly remove ethanol and benzene from shallow contaminated aquifers. Corseuil and Moreno (2001) used a similar lab set up as our fate and translocation study. Chang and colleagues (2005) also used a similar closed reactor system as in this dissertation. Chang et al., 2005, tested three species of poplar trees for the removal of atrazine from a growth medium (half-strength Hoaglands solution). Poplars were able to remove atrazine from the growth medium but had decreased growth rates as the concentrations of atrazine increased. The major objectives of this fate and translocation study were:

1. To trace the movement of cumene and 4-cumylphenol into *Salix nigra* cuttings using methods from Burken, 1996.

   * Results from the greenhouse phytotoxicity study showed that trace amounts of cumene were found attached to the roots of a *Salix nigra*, black willow.
2. To complete the material balance for translocation and fate of cumene and 4-cumylphenol via hydroponic mechanisms.
3. To provide a preliminary assessment for risk-based modeling of related phenolics removal using phytoremediation approaches.

MATERIALS AND METHODS

The study was conducted at Louisiana State University (LSU), Department of Environmental Sciences' lab. *Salix nigra* rooted cuttings were subjected to cumene and 4-cumylphenol using approaches based on work previously completed by Burken, 1996.

Rooted *Salix nigra* cuttings were selected from a batch of previously propagated cuttings. The soil was rinsed from the roots. The cuttings were cut approximately 30cm from the base of the stem. Because the study was initiated in December, the cuttings did not have leaves.

Approximately 10cm from the base of the stem the cuttings were wrapped with 1cm of Teflon tape. The Teflon tape was secured around the stem to prevent acrylic sealant from touching the stem. A modified screw top cap with Teflon liner was then securely placed over the Teflon wrapped stem. The screw top was sealed with acrylic sealant. The purpose of the tight seal was to prevent chemical transfer from the bottom flask to the top flask. This design would hypothetically only allow for transfer of chemicals from the bottom to top flask through the plant tissue.

The cutting was then placed in a screw top flask in half strength Hoaglands inorganic nutrient solution. A volume of 250mL of Hoaglands solution (in DI water) was poured into the

bottom flask. A modified 1L Erlenmeyer flask was fitted over the aerial portion of the cutting (top flask). The top flask was added three days after the acrylic sealant was dry to allow for diffusion of any chemicals from the sealant. Once the reactor was sealed cumene and 4-cumylphenol were spiked into the Hoagland solution at 30µg/mL, which equals 7,500µg/mL (in water, air, or tissue) for the total 250mL volume (250mL * 30µg/mL = 7500µg in 250mL).

The spike solution contained 5% methanol to allow the cumene and 4-cumylphenol to dissolve in the spike solution because cumene and 4-cumylphenol in the spike solution were at concentrations above that which would normally dissolve in water alone. Methanol is toxic to plants, but according to (Dorcus and Vivekanadan, 1996) methanol is not toxic to plants when it is below 15% of the concentration being applied to the plants. Our spike solution had methanol levels well below that of reported toxic levels.

A total of six reactors were used because of space limitations in the incubator. Two of the reactors were sealed with no cuttings (labeled A and B). The other four had *Salix nigra* cuttings (labeled C, D, E and F). The purpose of no cuttings (A and B) was to ensure that chemicals were not able to move from the bottom to the top flask through the sealant. All six reactors were placed in an incubator maintained at 20°C. A photoperiod of 16h/d and 8h/n was set using a standard 15 watt aquarium light bulb.

In order to determine a better mass balance of chemicals than the greenhouse experiment, the reactors had several outlets for sampling. The top flask had two outlets. One outlet was fitted with Tygon® tubing that allowed air pumped by an aquarium pump into the aerial portion of the microcosms. The other aerial outlet was fitted with Tygon® tubing that attached to an ORBO™ - 32 large charcoal tube (activated carbon trap). The A portion of the trap held any chemicals emitted into the aerial portion of the flask. The B portion of the trap showed a break through of chemicals from the trap. Therefore the A and B compartments were analyzed separately. All A

compartments were analyzed individually. The B compartments were analyzed together, but separated by A and B reactors (without cuttings) and C, D, E and F reactors (with cuttings).

The bottom flask was fitted with a Teflon lined septum to take water samples from. Since it was the water that was spiked with chemicals it was important to monitor chemical concentration in the water along with tissue and air samples. Figure 24 is a picture of the reactor.

Figure 24. Reactor Used to Determine the Fate of Cumene and 4-Cumylphenol in a Black Willow Cutting

Water Samples

Water samples from the bottom flask were collected at 0, 3, 6, 12, 24, 48, 96, 144, 192, and 216h; totaling a 10d study. Approximately 1mL of the water solution was removed from each flask for every designated sampling time. The 1mL of water solution was then placed into a vial with a Teflon top that had 1mL of DCM and 1mL of surrogate standard. The vials were then sonicated for 15min without heat. A volume of 0.2mL of the DCM was extracted from the vial using a graduated gas tight syringe. Internal standard at 10µg/mL was added and the sample was analyzed on the GC/MS using a modified EPA method 8270. A Hewlett Packard 5890 GC interfaced to an HP 5972 Mass Selective detector was used. The column was a J&W DB5 30mm

x 0.25mm x 0.25µm. the mass spectrometer was operated in select ion monitoring for cumene, 4-cumylphenol, and their metabolites.

Air Samples

Activated carbon samples were taken at 6, 12, 24, 48, 96, 144, 192, and 216h, again totaling a 10d study. Carbon traps were removed from the Tygon® tube and replaced with a new carbon trap at each sampling interval. The spent carbon tube was capped until extraction. Activated carbon was carefully removed from both the A and B portions of the trap. The activated carbon was placed in a 12mL glass vial with 2mL of carbon disulfide. The B vials had 4mL of carbon disulfide added to each vial because of the extra activated carbon. All vials were then placed on a shaker table for 2h at 100rpm. A volume of 0.8mL of the carbon disulfide was extracted from each vial and placed into a 2mL GC/MS autosampler Agilent crimp top vial. Internal standard at 10µg/mL was added to the vial prior to capping it. The samples were by GC/MS – SIM for the parent compounds and metabolites. The instrument acquisition and data processing methods were the same as water samples for determining the quantitative concentrations of the parent compounds and metabolites.

Tissue Samples

The plant tissue was separated into stems, leaves and roots and each were weighed and recorded. Sung et al. (2001) reported that several similar studies (Bruggemann, 1993; Trapp and Matthies, 1995; and Matthies and Behrendt, 1995) that divided the tested plants into one to three compartments for accessing the fate of contaminants within plants; Sung et al., 2001 found the one compartment model was too simple while the three compartment model was too complicated. When accessing TNT and chrysene uptake within Johnsongrass Sung and colleagues (2001) used a two compartment model. We are using a three compartment model (roots, stem, and leaves) to distinguish the portion of the plant in which cumene and 4-

cumylphenol translocate. The plant material was then placed into a 40mL vial with 15mL DCM and 1mL surrogate standard. The vial was sonicated for 10min. Meanwhile, funnels lined with Watson #2 filter paper were placed into funnels onto rotary evaporation flasks. The lined funnels were filled with anhydrous sodium sulfate, which removes any water present in the extract since it is a desiccant. The DCM was then poured over the anhydrous sodium sulfate and collected in a rotary evaporation flask. This process was repeated three times for each sample. The DCM in the rotary evaporation flasks was then concentrated to a 1mL sample on the rotary evaporator. The 1mL sample was then placed into a 2mL Agilent crimp top vial with 10µg/mL internal standard. The plant extractions were analyzed using the same instruments and methods as the water and air samples to determine quantitative concentrations of the parent compounds and metabolites.

The total concentration recovered in each reactor was calculated by first adding the concentration of cumene and 4-cumylphenol and all respective metabolites in the water, air and tissues for each individual reactor and each sampling interval. The total concentrations in each reactor for each sampling interval were then added together to get the total recovered concentration for that specific reactor. All percent recovery values are based on an initial spiked concentration of cumene and 4-cumylphenol at 7,500ng/mL.

RESULTS

Water Samples

Cumene, 4-cumylphenol, and metabolites were found in the water samples throughout the study. Because these chemicals were identified in concentrations above the calibration standard curve the linearity of the calibration standard (5 points) was determined using Chem. Station to calculate the R^2 for each individual analyte in the calibration standard. The R^2 values were as follows 0.998, 0.998, 0.996, 0.988, and 0.986 for cumene, acetophenone, DMBA, 4-cumylphenol, and phenanthrene-d_{10} respectively. All were very close to 1 or linear. Therefore we

can extrapolate lower or higher concentrations of these analytes with some confidence. Tables 33-35 give the concentrations of the individual parent and the metabolites (ng/mL) at each sampling interval.

Table 33. 4-Cumylphenol Present in Water at Individual Sampling Intervals

Sampling Interval (Hour)	Reactor					
	A	**B**	**C**	**D**	**E**	**F**
0	317.31	149.26	75.38	149.54	65.86	110.22
3	221.57	195.19	186.37	90.35	177.01	149.68
6	755.82	527.94	339.27	n.a.	323.68	385.07
12	1756.77	n.a.	1297.35	947.07	1234.62	919.22
24	790.49	876.64	594.98	396.90	792.20	n.a.
48	1545.38	628.24	435.31	420.73	463.74	905.23
96	272.83	14.58	6.45	4.37	14.91	11.40
144	874.73	0.00	0.00	0.00	0.00	0.00
192	785.83	597.23	196.68	452.96	168.74	519.27
216	0.00	0.00	0.00	0.00	0.00	0.00
Total	**7320.73**	**2989.08**	**3132.58**	**2464.43**	**3243.01**	**3004.65**

Values in table are reported in ng/mL. n.a. = not available because of surrogate recovery outside of the EPA limits 70-120%; GC oven malfunction; or loss of vial.

Approximately 98% of the 4-cumylphenol initially added to reactor A was recovered in the water. 40% of the 4-cumylphenol initially added to reactor B was identified in the water. 42% of the 4-cumylphenol initially added to reactor C was identified in the water. 33% of the 4-cumylphenol initially added to reactor D was identified in the water. 43% of the 4-cumylphenol initially added to reactor E was identified in the water. 40% of the 4-cumylphenol initially added to reactor F was identified in the water. Reactors C-F had rooted cuttings. Of the reactors with rooted cuttings, an average of 39.5% of the initially spiked 4-cumylphenol was identified in the water.

Approximately 70% of the cumene initially added to reactor A was identified in the water. 61% of the cumene initially added to reactor B was identified in the water. 78% of the cumene initially added to reactor C was identified in the water. 57% of the cumene initially

added to reactor D was identified in the water. 51% of the cumene initially added to reactor E was identified in the water. 68% of the cumene initially added to reactor F was identified in the water. Of the reactors with rooted cuttings, an average of 63.5% of the initially spiked cumene was identified in the water.

Table 34. Cumene Present in Water at Individual Sampling Intervals

Sampling Interval (Hour)	Reactor					
	A	**B**	**C**	**D**	**E**	**F**
0	2512.35	2634.17	2215.36	884.96	928.77	539.23
3	1307.49	676.05	1368.24	1032.63	1042.21	1002.67
6	655.03	360.03	754.20	n.a.	722.50	737.39
12	534.84	n.a.	757.52	585.18	518.29	642.52
24	126.37	61.32	356.71	333.90	185.75	321.67
48	27.75	36.25	87.20	135.78	98.55	n.a.
96	62.20	235.20	242.32	363.04	322.51	919.65
144	1.13	245.21	78.54	528.55	0.00	569.54
192	3.64	103.37	0.00	112.10	0.00	166.35
216	0.00	217.48	0.00	276.78	0.00	223.17
Total	**5230.80**	**4569.08**	**5860.23**	**4253.99**	**3818.72**	**5123.67**

Values in table are reported in ng/mL. n.a. = not available because of surrogate recovery levels outside of the EPA limits 70-120%; GC oven malfunction; or loss of vial.

Metabolites of cumene and 4-cumylphenol are slightly different. In aerated conditions cumene is thought to metabolize into DMBA, which further metabolizes into α-methylstyrene and water. In aerated conditions 4-cumylphenol is thought to metabolize into α-methylstyrene and phenol. The retention times and major ions of α-methylstyrene and phenol are very similar. Consequently, α- methylstyrene and phenol could not be resolved because of coelution. Therefore for cumene, the presence of both phenol and α-methylstyrene must be taken into account as potential metabolites.

If cumene only metabolized into DMBA and α-methylstyrene then approximately 5%, 4%, 4%, 3%, 9%, and 1.4% of these two metabolites account for the total initially spiked concentration of cumene added to reactor A, B, C, D, E and F respectively.

If cumene metabolized into acetophenone then approximately 0%, 2%, 0%, <1%, <1%, <1% of this metabolite accounted for the total initially spiked concentration of cumene added to reactor A, B, C, D, E, and F respectively.

Table 35. Metabolites Present in Water at Individual Sampling Intervals

Sampling Interval (Hour)	Metabolite	Reactor					
		A	B	C	D	E	F
0	Phenol / AMS	0.00	0.00	0.00	0.00	0.00	0.00
	Acetophenone	0.00	0.00	0.00	0.00	0.00	0.00
	DMBA	0.00	0.00	0.00	0.00	0.00	0.00
3	Phenol / AMS	0.00	0.00	0.00	0.00	0.00	0.00
	Acetophenone	0.00	0.00	0.00	0.00	0.00	0.00
	DMBA	0.00	0.00	0.00	0.00	0.00	0.00
6	Phenol / AMS	0.00	0.00	0.00	n.a.	0.00	0.00
	Acetophenone	0.00	0.00	0.00	n.a.	0.00	0.00
	DMBA	0.00	0.00	0.00	n.a.	0.00	0.00
12	Phenol / AMS	0.00	n.a.	0.00	0.00	0.00	0.00
	Acetophenone	0.00	n.a.	0.00	3.71	2.88	0.00
	DMBA	0.00	n.a.	0.00	0.00	0.00	0.00
24	Phenol / AMS	0.00	0.00	0.00	0.00	381.2	0.00
	Acetophenone	0.00	1.49	0.00	2.93	32.50	1.35
	DMBA	65.65	54.37	73.55	47.58	0.00	39.83
48	Phenol / AMS	1.44	0.00	4.02	0.95	0.00	n.a.
	Acetophenone	0.00	3.98	0.00	2.23	0.68	n.a.
	DMBA	97.29	49.97	58.40	25.63	74.25	n.a.
96	Phenol / AMS	0.00	0.00	0.00	0.00	0.00	0.00
	Acetophenone	0.00	42.83	0.00	0.00	0.00	0.00
	DMBA	0.00	0.00	0.00	0.00	0.00	0.00
144	Phenol / AMS	0.00	0.00	0.00	0.00	0.00	0.00
	Acetophenone	0.00	55.85	0.00	0.00	0.00	0.00
	DMBA	0.00	0.00	0.00	0.00	0.00	0.00
192	Phenol / AMS	0.00	0.00	0.00	0.00	0.00	0.00
	Acetophenone	0.00	11.98	0.00	7.34	0.00	3.64
	DMBA	239.14	175.06	200.74	146.91	252.52	70.15
216	Phenol / AMS	0.00	0.00	0.00	0.00	0.00	0.00
	Acetophenone	0.00	43.74	0.00	0.00	0.00	0.00
	DMBA	0.00	0.00	0.00	0.00	0.00	0.00
Total Metabolites	**ALL**	**403.52**	**439.27**	**336.71**	**237.28**	**744.03**	**114.97**

Values in table are reported in ng/mL. n.a. = not available because of surrogate recovery levels outside of the EPA limits 70-120%; GC oven malfunction; or loss of vial. AMS= α-methylstyrene

If 4-cumylphenol metabolized into α-methylstyrene and phenol then less than 1% of the initially spiked parent compounds were identified in reactors A, B, C, D, and F. Approximately 5% of the initially spiked parent compounds were identified in reactor E.

Air Samples

Cumene and 4-cumylphenol were not found in the air samples collected on the charcoal traps during all sampling periods. This result was expected as the log K_{ow}'s of both cumene and 4-cumylphenol indicate that the chemicals would not move into the xylem of the plant tissue and therefore would not be transpired from the leaves of the cuttings into the air.

To ensure that the readings were accurate and that the activated carbon traps were capable of absorbing cumene and 4-cumylphenol, four cumene / 4-cumylphenol blank reactors were analyzed. These reactors had no rooted cutting and no acrylic sealant or Teflon lining between the water and air being analyzed. Therefore if cumene and 4-cumylphenol evaporated from the water they would be free to diffuse to the aerial portion of the reactor and absorb to the activated carbon trap. The reactors were set up and spiked with both cumene and 4-cumylphenol at ten times the 30μg/mL rate of the experiment. The carbon traps were sampled 6h after the spike. Cumene, acetophenone, DMBA, and α – methylstyrene were identified on all 4 of the carbon traps. 4-Cumylphenol was identified on 1 of the 4 carbon traps. The large quantity of chemicals spiked into the water overloaded the column making quantification of the chemicals not reliable, but detectable. These results indicate that cumene and 4-cumylphenol do not readily evaporate from water but are detectable on the ORBO-32 large carbon traps.

Tissue Samples

Cumene and 4-cumylphenol were found in the cutting's root and stem tissue. The concentration of chemicals, both parent and metabolite, found in the tissue was marginal. Tables

36 and 37 display surrogate corrected amounts of the target analytes in individual root and stem tissue samples.

Two of the four rooted cuttings developed leaves in the 10d period. The presence of the parent chemicals and metabolites were not found in one of the leaf samples. The other leaf sample was lost because of a failure to maintain proper oven temperature during GC/MS analysis. Therefore this study is limited to the fate of the select chemicals in the root and stem tissue. However, if the chemicals were present in the leaf tissue it is hypothesized that they would also be found in the air samples.

Both the D and F rooted cuttings had close to 1ng/ml cumene located in the root tissue. 4-Cumylphenol was found at approximately 1ng/mL in the C rooted cutting and above 1ng/mL but no more than 4.5ng/mL in the other rooted cuttings. There was <1.0% of the total initial spiked concentration of cumene and 4-cumylphenol found in the plant tissue.

Table 36. Constituents of Concern Found in Root Tissue Samples.

Chemical	**Reactor**			
	c-root	**d-root**	**e-root**	**f-root**
	Conc (ng/mg)	**Conc. (ng/mg)**	**Conc. (ng/mg)**	**Conc. (ng/mg)**
Cumene	0.03	0.58	0.03	0.72
Phenol/methylstyrene	0.00	0.01	0.00	0.00
acetophenone	0.00	0.05	0.01	0.04
DMBA	0.00	0.31	0.06	0.11
4-Cumylphenol	0.84	0.96	1.31	4.07
Surrogate Recovery	0.90	0.80	0.90	0.92
Surrogate Corrected	**Conc. (ng/mg)**	**Conc. (ng/mg)**	**Conc. (ng/mg)**	**Conc. (ng/mg)**
Cumene	0.03	0.73	0.03	0.78
Phenol/methylstyrene	0.00	0.01	0.00	0.00
acetophenone	0.00	0.06	0.01	0.04
DMBA	0.00	0.39	0.07	0.12
4-Cumylphenol	0.93	1.20	1.46	4.42

Cumene and 4-cumylphenol quantities were even less in the stem samples. The F rooted cutting had the highest concentration of cumene at 0.59ng/mL and the D rooted cutting had the

highest concentration of 4-cumylphenol at 0.12ng/mL. Phenol and methylstyrene were not found in the stems, acetophenone was detected at a concentration less than 1.0ng/mL. DMBA was present in larger quantities than the parent compounds or other metabolites. Even so, <1% of the initially spiked parent compounds, cumene and 4-cumylphenol and metabolites were found in the stem tissue.

Table 37. Constituents of Concern Found in Stem Tissue Samples.

Chemical	Bioreactor			
	c-stem	d-stem	e-stem	f-stem
	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	0.07	0.30	0.09	0.56
Phenol/methylstyrene	0.00	0.00	0.01	0.00
acetophenone	0.02	0.11	0.14	0.08
DMBA	0.19	0.75	1.55	0.59
4-Cumylphenol	0.00	0.11	0.02	0.02
Surrogate Recovery	1.17	0.93	0.97	0.95
Surrogate Corrected	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)	Conc. (ng/mg)
Cumene	0.06	0.32	0.09	0.59
Phenol/methylstyrene	0.00	0.00	0.01	0.00
acetophenone	0.01	0.12	0.15	0.09
DMBA	0.16	0.80	1.60	0.62
4-Cumylphenol	0.00	0.12	0.02	0.02

Concentration Balance

The total concentration identified of cumene and 4-cumylphenol is presented in Tables 38 and 39 respectively. These tables take into account the chemicals found in both water and plant tissue samples. Air samples are not factored into the tables because cumene, 4-cumylphenol, nor their presumed metabolites were identified in the air samples.

Percent recovery of cumene was moderately high depending on the possible analytes metabolized. If cumene broke only into DMBA and α- methylstyrene then 75%, 65%, 83%, 60%, 60%, and 70% of the total initial spiked concentration of cumene was identified throughout the reactors for reactors A, B, C, D, E and F respectively. If cumene broke only into

acetophenone then 70%, 63%, 78%, 60%, 51%, and 68% of the total concentration of initially spiked cumene was identified throughout the reactors in reactors A, B, C, D, E and F respectively.

Table 38. Total Concentration of Cumene Identified in the Lab Study

		Reactor					
Chemical	**Sample**	**A**	**B**	**C**	**D**	**E**	**F**
Cumene	**W**	5230.80	4569.08	5860.23	4253.99	3818.72	5123.67
Cumene	**T**	n.a.	n.a.	0.09	1.05	0.12	1.37
Metabolite (DMBA and AMS)	**W**	403.52	279.4	336.71	221.07	707.97	109.98
Metabolite (Acetophenone)	**W**	0.00	159.87	0.00	16.21	36.06	4.99
Metabolite (DMBA and AMS)	**T**	n.a.	n.a.	0.16	1.20	1.68	0.74
Metabolite Acetophenone	**T**	n.a.	n.a.	0.01	0.18	0.16	0.13
Mass Total Plant analytes + DMBA and AMS	**All**	**5634.32**	**4848.48**	**6197.19**	**4477.31**	**4528.49**	**5235.76**
Mass Total Plant analytes + Acetophenone	**All**	**5230.80**	**4728.95**	**5860.33**	**4271.43**	**3855.06**	**5130.16**

Values in table are reported in ng/mL for water samples and ng/mg for tissue samples. n.a. = not available because tissue samples were not sampled for reactors A and B. AMS = α-methylstyrene. W = Water. T= Tissue. Tissue sample totals include chemicals found in both roots and stems.

Percent recovery of 4-cumylphenol was less than cumene except in reactor A. Including AMS and phenol as potential metabolites of 4-cumylphenol, the percent recovery of the total mass of initially spiked 4-cumylphenol in each reactor was 98%, 40%, 42%, 33%, 48%, and 40% in reactors A, B, C, D, E and F respectively.

Table 39. Total Concentration of 4-Cumylphenol Identified in the Lab Study

		Reactor					
Chemical	**Sample**	**A**	**B**	**C**	**D**	**E**	**F**
4-CP	**W**	7320.73	2989.08	3132.58	2464.43	3243.01	3004.65
4-CP	**T**	n.a.	n.a.	0.93	1.32	1.48	4.44
Metabolite AMS + phenol	**W**	1.44	0.00	4.02	0.95	381.2	0.00
Metabolite (AMS + phenol)	**T**	n.a.	n.a.	0	0.01	0.01	0
Mass Total including AMS + phenol	**All**	**7322.17**	**2989.08**	**3137.53**	**2466.71**	**3625.70**	**3009.09**

Values in table are reported in ng/mL for water samples and ng/mg for tissue samples. n.a. = not available because tissue samples were not sampled for reactors A and B. AMS = α-methylstyrene. 4-CP = 4-cumylphenol. W = Water. T= Tissue. Tissue sample totals include chemicals found in both roots and stems.

CONCLUSIONS

The total mass of the constituents of concern added to the reactors was not accounted for at the end of the 10d study. The majority of the chemicals were detected in the water and a small amount was identified in the tissue samples, both roots and stem. Two of four cuttings developed leaves. The leaf samples were too small for accurate measurements of chemical content. When leaf samples were analyzed, the results were below acceptable EPA surrogate recovery levels (70-120%) and therefore, cannot be reliably used.

The average percent of initially spiked cumene recovered in all 6 reactors was 68% if the metabolites DMBA and α-methylstyrene were used and 65% if the metabolite acetophenone was factored into the mass total. The average percent of initially spiked 4-cumylphenol recovered in all 6 reactors was 50% using α-methylstyrene and phenol as the presumed metabolites.

There are two possibilities to explain the missing percentage of chemical concentration. The first hypothesis is that the chemicals may have evaporated from the water into the headspace above the water in the bottom flask. The reactors did not have a sampling port in this location to

add an additional carbon trap. The second hypothesis is that the remaining percentage of chemicals was actually in the water. A 1mL sample of water was taken at each sampling interval with the last sampling interval at 216h. Only 1mL of water was extracted at 216h and the remaining water was discharged. In hindsight it would have been best to sample the remainder of the water in each reactor.

If this study were repeated, two additional steps would need to be completed for a better account of the concentration balance of chemicals. First, the reactors would need to be modified with two additional sampling ports on the bottom flask, one for air intake and one for the additional carbon trap. Second, at the end of the study, instead of extracting 1mL of the water, purge and extract all the remaining water to determine total chemical concentration in the water.

However, it was conclusive that in as little as 10d, the root system of trees can begin to translocate both cumene and 4-cumylphenol. A longer study period would better determine the total amount of chemicals that could be translocated into the tree tissue. The immediate uptake occurred because the presence of chemicals was present directly within the root zone of the cuttings. In the full scale planting, phytoremediation will take more time because roots will have to grow to depths of 10 to 22 feet before coming in contact with the COC's.

This study was completed over a period of ten days. An extended sampling period may show a higher accumulation of the parent chemicals in the root tissue. The metabolites in root samples were found in minimal amounts.

CHAPTER 9

OVERALL CONCLUSIONS

OVERALL CONCLUSIONS

Description of Experiments

Three studies were conducted to determine the feasibility of using phytoremediation as a means to remediate a contaminated groundwater plume. The first study consisted of two consecutive greenhouse trails to determine an optimum tree species that would survive contact with the chemicals of concern, survive contact with the high NaCl levels in the groundwater plume, and potentially remediated the contaminated groundwater plume through the mechanisms of rhizodegradation, phytostabilisation, and hydraulic control.

The second study was conducted to determine the toxicity of cumene and 4-cumylphenol on higher order plant species. There is relatively little information on the toxicity of these chemicals to plants. A Phytotoxkit™ was used to access chemical effects on seed germination and radical length of three plant species when in contact with contaminated soil water.

The third study that was conducted was a fate and translocation study of cumene and 4-cumylphenol through black willow cuttings. The cuttings were placed in closed reactor systems. After closed, the reactors were spiked with cumene and 4-cumylphenol. Water, air, and tissue were sampled throughout the study to determine the fate and translocation of the chemicals within the cuttings.

Greenhouse Results

Results from the greenhouse studies indicated that the both the black willow and bald cypress trees were acceptable species for phytoremediation of cumene and 4-cumylphenol. The black willow trees were the highest water users and had the highest concentrations of cumene and 4-cumylphenol in their root tissue at the ends of the studies. The black willow trees were not affected by the COC water treatments in year one or two. However, in year one, the black willows were stunted in the 100% NaCl water treatment. The bald cypress was the chosen tree

species for full scale planting over the contaminated groundwater plume. The bald cypress was chosen because it was not significantly affected by either the COC or NaCl water treatments in year one and year two. The bald cypress was not severely impacted by insects or disease. The bald cypress was able to accumulate some cumene and 4-cumylphenol into its root tissue. The bald cypress grows in a conical form allowing close spacing of trees. It can be hedged which is a feature that complies with security monitoring requirements at the chemical facility. The bald cypress has a longer tap root system compared to the black willow, which should eventually reach the contaminated groundwater plume depths of 3.05 to 6.71m below ground surface.

Toxicity Test Results

Results from the second study indicated that at the historically highest recorded concentrations of cumene and 4-cumylphenol in the contaminated groundwater plume did not have a significant effect on seed germination nor radical length of the tested higher order plant species. The same chemicals at higher concentrations of 25 and 50ug/mL in soil water did not negatively impact seed germination or radical length. The lowest observable adverse effect level (LOAEL) was not determined in this study. The chemicals are insoluble in water at higher concentrations than those used in this study. If higher concentrations were used, a solvent would have to be added to the soil water. The addition of a solvent could have confounded results indicating effects of the solvent on seed germination and radical length rather than effects of the presence of cumene and 4-cumylphenol.

Fate and Translocation Results

Results from the third study, the fate and translocation of cumene and 4-cumylphenol in black willow cuttings, indicated that cumene and 4-cumylphenol could be translocated into black willow cuttings. Throughout the study water and air samples were collected. Plant tissue samples were collected at the end of the study. The majority of the mass of the chemicals remained in the

water throughout the study. Cumene and 4-cumylphenol were translocated into the root and stem tissue. Although concentration of chemicals found in the stem tissue was minimal, they were detectable. This finding was surprising as previous models indicated that chemicals with a log K_{ow} greater than 3.5 will not enter the xylem of a plant and therefore should not translocate out of the root tissue and into the stem and leaf tissue. The results from this study indicated that for some chemicals previous models may not be accurate as cumene's log K_{ow} is 3.66 and 4-cumylphenol's log K_{ow} is 4.12. Although detectable in root and stem tissue, these chemicals were not detected in the air samples during the study. The fate and translocation study was a preliminary study to access the translocation of cumene and 4-cumylphenol within a rooted cutting. The model and methods used in this study warrant further evaluation and trials before concluding publishable results.

Recommendations for Future Research

All studies in this dissertation suggest that phytoremediation is a feasible method of remediation of cumene and 4-cumylphenol contaminated groundwater. Further research should include experiments that produce the exact fate and translocation of these chemicals within a plant. The closed reactor system used in this study could be modified and replicated several times to produce accurate data on the fate of cumene and 4-cumylphenol in a plant's tissue. One specific area that should be researched is the log K_{ow} of these two chemicals. Previously published models indicate that chemicals with log K_{ow} values between 1.0 and 3.5 will translocate into a plants tissue. While those chemicals with log K_{ow}s above 3.5 will not translocate into the xylem of the plant and will probably not pass the root membrane (IRTC, 1999). However, in the fate and translocation study of this dissertation, both cumene and 4-cumylphenol (with log K_{ow} values above this range) were found in the root and stem tissue suggesting that the critical translocation log K_{ow} range may need to include higher values.

The toxicity study in this dissertation concluded that cumene and 4-cumylphenol do not have any significantly negative affects on seed germination and radical length at concentrations as high as 50µg/mL in soil water. Further evaluations should be made to determine a no observable adverse effect level (NOAEL) and lowest observable adverse effect level (LOAEL) of these two chemicals on plants. This information would define a concentration range at which phytoremediation would become a recommended remediation method for future cumene and 4-cumylphenol spills.

There has been little research on the toxicity levels of cumene and 4-cumylphenol. Additional research on toxicity levels as well as ultimate fate and translocation of these two chemicals within plant tissue would benefit those who study phytoremediation of volatile and semi-volatile organic compounds. Additional research would provide the needed data to promote phytoremediation as an acceptable *in-situ* method of remediation for cumene and 4-cumylphenol spills.

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APPENDIX: SUPPLIMENTARY DATA

Closed and Capped Impoundment Area Organic Pond Illustrations

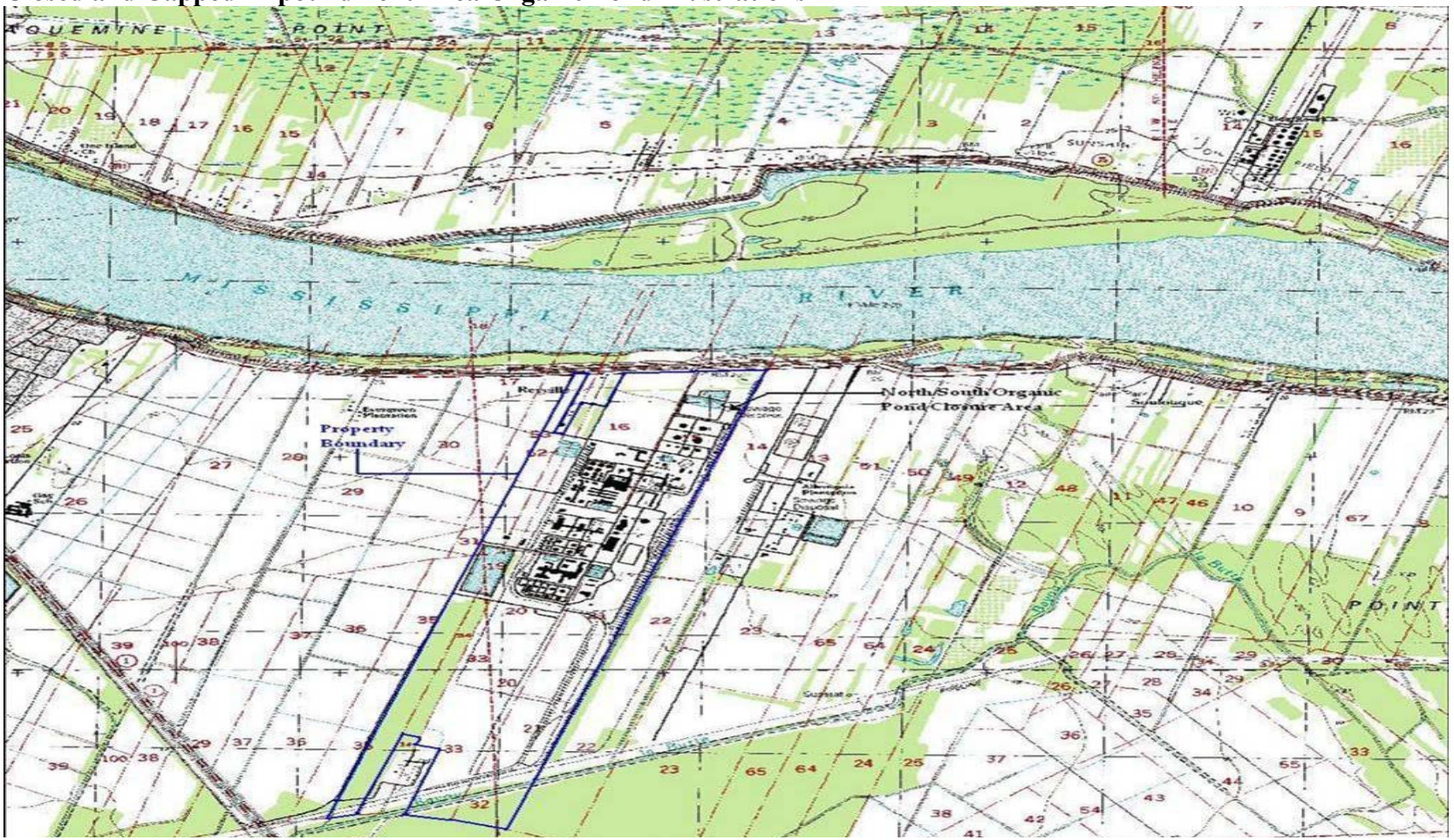

Figure A-1. Location of North South Organic Pond

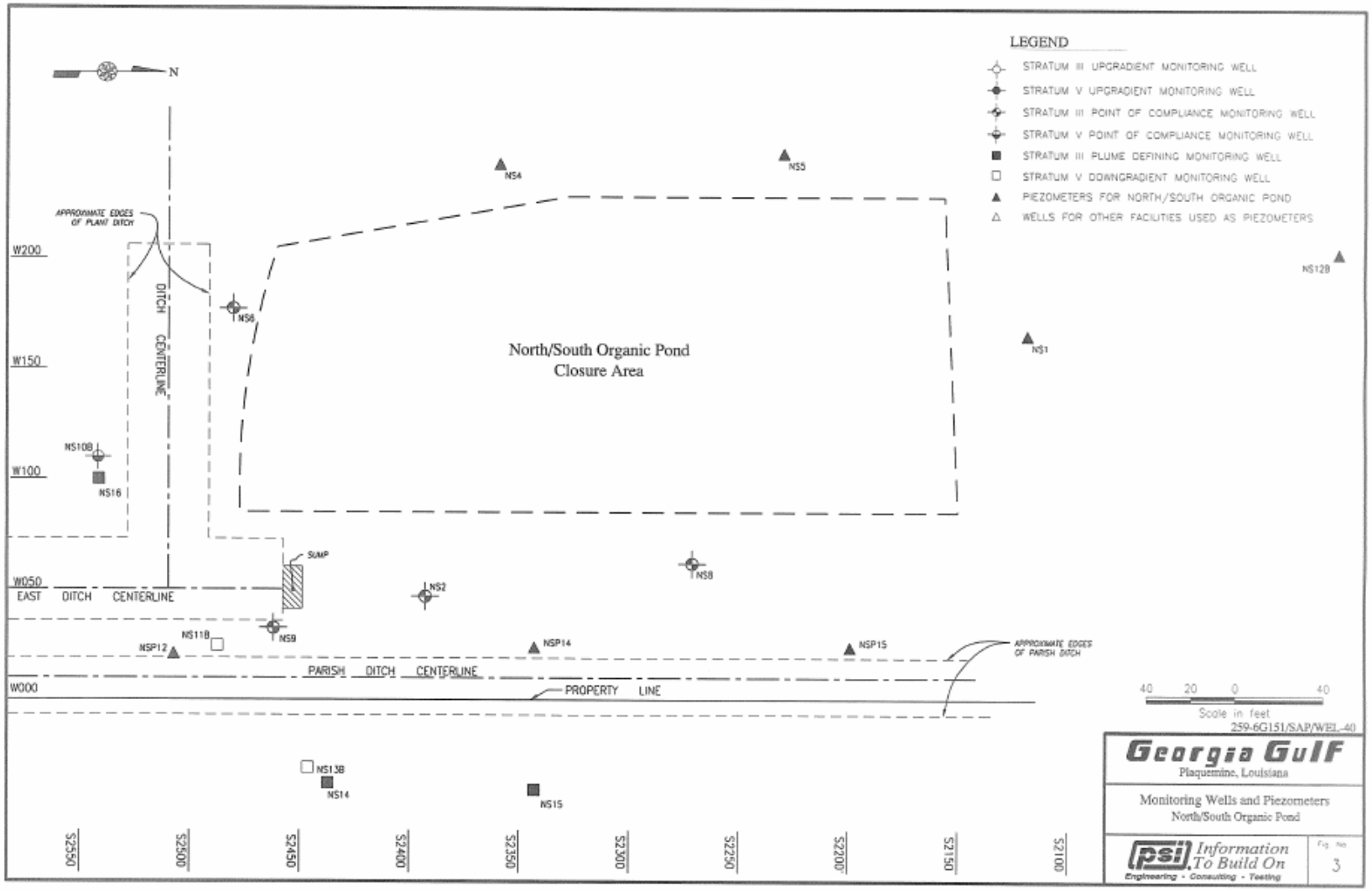

Figure A-2. The North South Organic Pond Closure Area

Figure A-3. Before end walls were constructed

Figure A-4. After construction of end walls

Figure A-5. 208.19 liter treatment tanks

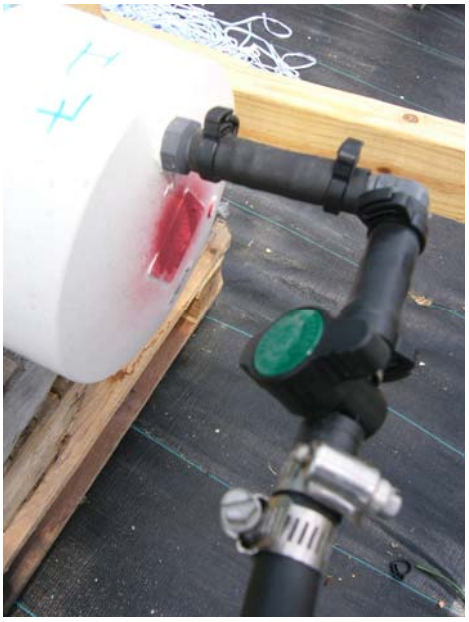

Figure A-6. and A-7. Input side of troughs

Figure A-8. Discharge end of trough

Figure A-9. Discharge Sump Tank

Figure A-10. Troughs with trees

Year 1 Plant Tissue Target Compounds

Table AB.1. Year 1 Target Compounds in Final Plant Tissue Samples

Water Trt	Sample Type	% Solids	Cumene (mg/kg)	4-Cumylphenol (mg/kg)	Acetophenone (mg/kg)	α, α-DMBA (mg/kg)	α-Methylstyrene (mg/kg)	Phenol (mg/kg)
Bald cypress								
Control	tops	44.7	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Control	tops	37.9	< 0.0029	< 0.076	< 0.033	< 0.032	< 0.037	< 0.050
Control	roots	22.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Control	roots	32.7	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	tops	43.8	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	tops	38.0	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	tops	40.1	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	tops	43.2	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	roots	28.2	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	roots	20.0	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	roots	25.5	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	roots	28.8	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100%COC	roots	21.0	< 0.0029	< 0.120	< 0.050	< 0.049	< 0.058	< 0.076
67% COC	tops	40.5	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	tops	41.0	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	tops	38.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	tops	49.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	roots	21.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	roots	28.3	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	roots	31.1	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	roots	30.3	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
33% COC	tops	50.9	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
33% COC	tops	38.9	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
33% COC	roots	32.3	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
33% COC	roots	26.4	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025

Table continued

Water Trt	Sample Type	% Solids	Cumene (mg/kg)	4-Cumylphenol (mg/kg)	Acetophenone (mg/kg)	α, α-DMBA (mg/kg)	α-Methylstyrene (mg/kg)	Phenol (mg/kg)
33% COC	roots	26.7	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
33% COC	roots	19.4	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Black willow								
Control	tops	57.5	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.460
Control	tops	44.7	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Control	roots	16.5	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.150
Control	roots	18.7	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.120 J
100% COC	tops	46.1	< 0.0030	< 0.042	< 0.018	< 0.018	< 0.021	0.280
100% COC	tops	40.3	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	0.530
100% COC	tops	41.1	< 0.0029	< 0.051	< 0.022	<0.021	< 0.025	0.720
100% COC	tops	54.3	< 0.0029	< 0.076	< 0.033	< 0.032	<0.037	0.710
100% COC	roots	17.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	roots	16.2	0.0054 J	0.130	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	roots	13.7	< 0.0030	0.086 J	< 0.016	< 0.016	< 0.019	0.089 J
67% COC	tops	55.5	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.280
67% COC	tops	48.2	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.240
67% COC	tops	50.3	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	tops	44.3	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.250
67% COC	roots	14.5	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.038 J
67% COC	roots	11.7	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	roots	13.7	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
67% COC	roots	14.2	< 0.00059	0.093 J	< 0.016	< 0.016	< 0.019	0.061 J
33% COC	tops	42.1	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.590
33% COC	tops	53.5	< 0.00059	< 0.051	< 0.022	< 0.021	< 0.025	0.700
33% COC	roots	13.2	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	0.310
33% COC	roots	22.4	< 0.00059	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Eastern red cedar								
Control	tops	42.5	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Control	tops	41.9	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025

Table continued

Water Trt	Sample Type	% Solids	Cumene (mg/kg)	4-Cumylphenol (mg/kg)	Acetophenone (mg/kg)	α, α-DMBA (mg/kg)	α-Methylstyrene (mg/kg)	Phenol (mg/kg)
Control	roots	19.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Control	roots	21.8	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	tops	45.0	< 0.0029	< 0.040	< 0.017	< 0.017	< 0.020	< 0.026
100% COC	tops	45.0	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	tops	45.9	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	tops	44.2	< 0.0029	< 0.048	< 0.020	< 0.020	< 0.023	< 0.031
100% COC	roots	19.5	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	roots	25.9	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Water Oak								
Control	tops	58.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
Control	tops	55.8	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	tops	55.5	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	tops	45.0	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	tops	53.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	tops	55.1	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	roots	34.5	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	roots	55.5	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	roots	37.8	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025
100% COC	roots	38.6	< 0.0029	< 0.038	< 0.016	< 0.016	< 0.019	< 0.025

Year 1 Final Media Target Compounds

Table AB.2. Year 1 Target Compounds in Final Potting Media Samples

Species	Treatment	% Solids	Cumene (mg/kg)	4-Cumylphenol (mg/kg)	Acetophenone (mg/kg)	α, α-DMBA (mg/kg)	α-Methyl styrene (mg/kg)	Phenol (mg/kg)
Bald cypress	Control	63.8	<0.00008	<0.330	<0.0986	<0.330	<0.330	0.108 J
	Control	74.1	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	69.1	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	70.0	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	71.8	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	71.2	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	71.7	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	67% COC	66.7	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	67% COC	70.8	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	67% COC	70.0	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	67% COC	69.3	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	33% COC	66.7	<0.00008	<0.330	<0.0986	<0.330	<0.330	0.0837 J
	33% COC	65.2	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	33% COC	73.0	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	33% COC	70.9	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
Black willow	Control	71.1	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	Control	74.2	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	74.3	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	74.3	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	75.9	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	73.6	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	71.1	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	67% COC	73.4	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	67% COC	71.4	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	67% COC	71.4	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697

Table continued

Species	Treatment	% Solids	Cumene (mg/kg)	4-Cumylphenol (mg/kg)	Acetophenone (mg/kg)	α, α-DMBA (mg/kg)	α-Methyl styrene (mg/kg)	Phenol (mg/kg)
	67% COC	72.3	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	33% COC	73.4	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	33% COC	70.6	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	33% COC	72.3	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	33% COC	71.5	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
Eastern red cedar	Control	66.3	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	Control	68.2	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	71.1	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	65.4	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	66.0	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	64.4	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
Water oak	Control (7)	77.2	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	Control (8)	64.8	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	67.3	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	67.6	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	74.6	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697
	100% COC	77.0	<0.00008	<0.330	<0.0986	<0.330	<0.330	<0.0697

Note: Concentrations are reported on a wet basis. NS = not sampled.

Year 2 Target Compounds in Plant Tissue Samples

Table AB.3 Year 2 Target Compounds in Final Root Tissue Samples

Species Name	Trt	Sample Type	% Solids	Cumene (mg/kg)	4-Cumyl-phenol (mg/kg)	Acetophenone (mg/kg)	α, α-DMBA (mg/kg)	α-Methyl-styrene (mg/kg)	Phenol (mg/kg)
Bald Cypress	Control	roots	84.2	< 0.0530	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	78.9	< 0.0520	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	80.9	< 0.0525	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	76.2	< 0.0520	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	86.0	< 0.0530	0.939	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	80.1	< 0.0525	0.678	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	75.5	< 0.0530	1.13	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	79.7	< 0.0520	4.12	< 0.0688	< 0.0901	< 0.107	< 0.0625
	High	roots	83.6	< 0.0510	1.52	< 0.0688	< 0.0901	< 0.107	< 0.0625
	High	roots	76.7	< 0.0515	1.50	< 0.0688	< 0.0901	< 0.107	< 0.0625
	High	roots	66.5	< 0.0510	2.27	< 0.0688	< 0.0901	< 0.107	< 0.0625
	High	roots	79.9	< 0.0525	0.690	< 0.0688	< 0.0901	< 0.107	< 0.0625
Black Willow	Control	roots	69.4	< 0.0525	0.383 J	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	70.1	< 0.0520	0.208 J	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	74.1	< 0.0530	0.208 J	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	73.0	< 0.0525	0.0976 J	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	72.9	< 0.0530	14.4	< 0.275	< 0.360	< 0.427	< 0.250
	Low	roots	69.6	< 0.0530	21.5	< 0.344	< 0.451	< 0.533	< 0.312
	Low	roots	73.6	< 0.0520	13.7	< 0.275	< 0.360	< 0.427	< 0.250
	Low	roots	70.9	< 0.0520	16.7	< 0.344	< 0.451	< 0.533	< 0.312
	High	roots	76.3	< 0.0505	35.7	< 0.550	< 0.721	< 0.853	< 0.500
	High	roots	76.7	< 0.0525	4.61	< 0.0688	0.117 J	< 0.107	< 0.0625
	High	roots	77.3	< 0.0510	20.4	< 0.275	< 0.360	< 0.427	< 0.250
	High	roots	77.5	< 0.0520	24.0	< 0.275	0.567 J	< 0.427	< 0.250
	High	roots	77.4	< 0.0520	22.5	< 0.275	0.409 J	< 0.427	< 0.250

Table continued

Species Name	Trt	Sample Type	% Solids	Cumene (mg/kg)	4-Cumyl-phenol (mg/kg)	Acetophenone (mg/kg)	α, α-DMBA (mg/kg)	α-Methyl-styrene (mg/kg)	Phenol (mg/kg)
Cotton-wood	Control	roots	80.3	< 0.0520	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	71.1	< 0.0510	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	77.3	< 0.0515	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Control	roots	80.7	< 0.0520	< 0.0461	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	78.2	< 0.0525	3.42	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	80.3	< 0.0525	1.25	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	79.8	< 0.0525	0.403 J	< 0.0688	< 0.0901	< 0.107	< 0.0625
	Low	roots	71.8	< 0.0525	0.875	< 0.0688	< 0.0901	< 0.107	< 0.0625
	High	roots	77.6	< 0.0520	1.26	< 0.0688	< 0.0901	< 0.107	< 0.0625
	High	roots	79.3	< 0.0520	7.63	< 0.138	0.935 J	< 0.213	< 0.125
	High	roots	83.6	< 0.0525	5.35	< 0.138	0.319 J	< 0.213	< 0.125
	High	roots	68.7	< 0.0525	0.870	< 0.0688	< 0.0901	< 0.107	< 0.0625

Note: Concentrations are reported on a wet weight basis. "J flag" indicates an estimated concentration below the Practical Quantitation Limit (PQL).

Year 1 – Initial Plant Tics

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Black Willow Roots

VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Value	Chemical Name	Chemical Formula	CAS No.
VOC	1.86	0.031	78	1-Propene, 2-methyl-	C4H8	115-11-7
SVOC	8.06	1.6	40	Unknown	n/a	n/a
SVOC	16.31	1.1	43	Unknown	n/a	n/a
SVOC	19.30	1.3	47	Unknown	n/a	n/a
SVOC	22.01	0.87	45	Unknown	n/a	n/a
SVOC	22.08	1.9	32	Unknown	n/a	n/a
SVOC	23.86	13	30	Unknown	n/a	n/a
SVOC	8.06	2.1	38	Unknown	n/a	n/a
SVOC	13.01	1.2	90	Decanoic acid, methyl ester	C11H2202	110-42-9
SVOC	8.02	0.91	42	Unknown	n/a	n/a
SVOC	12.95	1.1	93	Hexadecanoic acid, methyl ester	C17H34O2	112-39-0
SVOC	18.38	0.82	78	Unknown	n/a	n/a
SVOC	18.43	0.88	46	Unknown	n/a	n/a
SVOC	19.20	1.0	43	Unknown	n/a	n/a
SVOC	22.19	1.3	42	Unknown	n/a	n/a
VOC	1.87	0.032	64	1-Propene, 2-methyl-	C4H8	115-11-7
SVOC	5.85	1.2	96	Benzaldehyde, 4-hydroxy-	C7H6O2	123-08-0
SVOC	8.05	0.98	38	Unknown	n/a	n/a
SVOC	8.79	0.89	37	Unknown	n/a	n/a
SVOC	13.00	0.81	83	Tridecanoic acid, methyl ester	C14H28O2	1731-88-0

Table Continued

VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Value	Chemical Name	Chemical Formula	CAS No.
SVOC	17.33	1.1	59	Unknown	n/a	n/a
SVOC	18.52	1.4	43	Unknown	n/a	n/a
SVOC	5.85	0.82	87	Benzeneacetaldehyde	C8H8O	122-78-1
SVOC	8.07	2.2	40	Unknown	n/a	n/a
SVOC	17.34	0.87	25	Unknown	n/a	n/a
SVOC	19.31	1.1	51	Unknown	n/a	n/a
SVOC	23.42	2.9	64	Unknown	n/a	n/a

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Black Willow Tops

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
3.67	TBLACKW01	0.73	Hexanal	C6H12O	66-25-1	90
3.67	TBLACKW02	0.85	Hexanal	C6H12O	66-25-1	90
4.18	TBLACKW01	6.7	2-Hexenal, (E)-	C6H10O	6728-26-3	97
4.18	TBLACKW02	7.0	2-Hexenal, (E)-	C6H10O	6728-26-3	97
4.27	TBLACKW01	1.1	2-Hexen-1-ol, (E)-	C6H12O	928-95-0	91
4.27	TBLACKW02	0.97	Cyclohexanol	C6H12O	108-93-0	86
5.46	TBLACKW01	2.2	Unknown			83
5.46	TBLACKW02	2.0	Unknown			83
5.59	TBLACKW01	3.9	Unknown			78
5.59	TBLACKW02	5.8	Unknown			72
5.74	TBLACKW01	1.6	Unknown			64
5.80	TBLACKW01	18.0	Unknown			81
5.81	TBLACKW02	20.0	Unknown			72
5.87	TBLACKW01	2.0	Benzenemethanol (Benzyl Alcohol)	C7H8O	100-51-6	98
5.87	TBLACKW02	2.1	Benzenemethanol (Benzyl Alcohol)	C7H8O	100-51-6	98
5.90	TBLACKW01	1.6	1,4-Dichlorobenzene-d4	C6C12D4	3855-82-1	96
6.00	TBLACKW01	2.8	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8	96
6.00	TBLACKW02	2.0	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8	97
6.16	TBLACKW01	4.1	1,2-Cyclohexanediol, trans-	C6H12O2	1460-57-7	95
6.15	TBLACKW02	2.7	1,2-Cyclohexanediol, trans-	C6H12O2	1460-57-7	94
6.31	TBLACKW01	13.0	1,2-Cyclohexanediol, trans-	C6H12O2	1460-57-7	95
6.44	TBLACKW01	1.7	Benzoic acid, methyl ester	C8H8O2	93-58-3	94

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
8.13	TBLACKW01	2.4	Salicyl Alcohol	C7H8O2	90-01-7	95
8.14	TBLACKW02	2.2	Salicyl Alcohol	C7H8O2	90-01-7	95
8.68	TBLACKW01	1.6	Unknown			78
8.69	TBLACKW02	2.4	Unknown			78
8.76	TBLACKW01	2.7	Eugenol	C10H12O2	97-53-0	97
8.77	TBLACKW02	3.9	Eugenol	C10H12O2	97-53-0	97
8.91	TBLACKW01	1.0	4-Methoxyphenethyl Alcohol	C9H12O2	702-23-8	94
8.92	TBLACKW02	1.4	4-Methoxyphenethyl Alcohol	C9H12O2	702-23-8	95
8.99	TBLACKW01	0.79	2-Propenoic acid, 3-phenyl-, methyl ester	C10H10O2	103-26-4	96
9.00	TBLACKW02	0.94	2-Propenoic acid, 3-phenyl-, methyl ester	C10H10O2	103-26-4	97
9.32	TBLACKW01	0.82	Unknown			64
9.33	TBLACKW02	1.6	Unknown			70
9.44	TBLACKW02	0.62	Ethanone, 1-(4-hydroxyphenyl)	C8H8O2	99-93-4	95
9.61	TBLACKW02	0.6	Cyclododecane	C12H24	294-62-2	96
11.77	TBLACKW01	2.3	2-Propenoic acid, 3-(3-hydroxyphenyl)-methyl ester	C10H10O3	3943-95-1	94
11.77	TBLACKW02	1.9	2-Propenoic acid, 3-(3-hydroxyphenyl)-methyl ester	C10H10O3	3943-95-1	93
21.91	TBLACKW01	30.0	Stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6	98
21.90	TBLACKW02	25.0	Stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6	91
22.65	TBLACKW01	4.0	Unknown			78

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Bald Cypress Roots

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
5.46	RBALDC01	3.7	Unknown			83
5.46	RBALDC02	3.0	Unknown			83
7.11	RBALDC01	1.8	Borneol	C10H18O	507-70-0	87
7.11	RBALDC02	1.2	Borneol	C10H18O	507-70-0	93
9.13	RBALDC01	0.66	Vanillin	C8H8O3	121-33-5	97
9.60	RBALDC01	1.2	Cyclododecane	C12H24	294-62-2	97
9.60	RBALDC02	0.91	1-Decene	C10H20	872-05-9	95
11.77	RBALDC01	9.2	Unknown			43
11.75	RBALDC02	3.6	Unknown			46
14.29	RBALDC02	1.0	Unknown			53
14.49	RBALDC01	1.0	Unknown			59
14.49	RBALDC02	1.2	Unknown			70
15.53	RBALDC01	9.8	Unknown			83
15.53	RBALDC02	11.0	1,4,8-Trimethoxyanthracen-9-ol	C17H16O4	80893-75-0	90
15.56	RBALDC01	4.0	4,4-Dimethyl-13.alpha.-androst-5-ene	C21H34	73495-94-0	90
15.56	RBALDC02	5.0	4,4-Dimethyl-13.alpha.-androst-5-ene	C21H34	73495-94-0	90
15.64	RBALDC01	2.1	Unknown			64
15.64	RBALDC02	1.6	Unknown			68
15.98	RBALDC01	0.84	Unknown			64
16.28	RBALDC02	0.61	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1,1,4a-trimethyl-7-(1-methylethyl)	C21H32O	10064-26-3	89
16.91	RBALDC02	0.72	Unknown			74
17.18	RBALDC01	0.89	9(1H)-Phenanthrenone, 2,3,4,4a,10,10a-hexahydro-	C20H28O2	511-05-7	95

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
17.18	RBALDC02	0.95	9(1H)-Phenanthrenone, 2,3,4,4a,10,10a-hexahydro-6-hydroxy-1,1,4a-trimethyl-7-(1-methylethyl)	C20H28O2	511-05-7	96
21.28	RBALDC01	0.89	Ergost-5-en-3.beta.-ol	C28H48O	0-00-0	90
21.48	RBALDC01	0.86	Unknown			47
21.88	RBALDC01	4.2	Stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6	99
21.89	RBALDC02	4.0	Unknown			74

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Bald Cypress Tops

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
3.66	TBALDC01	7.9	Furan, tetrahydro-3-methyl-4-methylene-	C6H10O	61142-01-6	87
3.67	TBALDC02	2.2	Hexanal	C6H12O	66-25-1	86
4.17	TBALDC01	13.0	2-Hexenal, (E)-	C6H10O	6728-26-3	95
4.18	TBALDC02	6.5	2-Hexenal, (E)-	C6H10O	6728-26-3	96
4.29	TBALDC01	2.2	1-Hexanol	C6H14O	111-27-3	90
4.87	TBALDC02	3.5	Tricyclo[2.2.1.02,6]heptane, 1,7,7-trimethyl-	C10H16	508-32-7	96
4.99	TBALDC01	41.0	Cyclohexene, 1-methyl-4-(1-methylehtenyl)	C10H16	5989-27-5	97
5.03	TBALDC01	1.8	Unknown			53
5.06	TBALDC02	96.0	.alpha. Pinene	C10H16	80-56-8	96
5.14	TBALDC02	3.6	Camphene	C10H16	79-92-5	98
5.36	TBALDC01	6.1	2-.beta.-Pinene	C10H16	127-91-3	95
5.38	TBALDC02	9.0	2-.beta.-Pinene	C10H16	127-91-3	97
5.43	TBALDC01	8.4	.beta.-Myrcene	C10H16	123-35-3	97
5.44	TBALDC02	14.0	.beta.-Myrcene	C10H16	123-35-3	94
5.47	TBALDC01	2.6	Unknown			83
5.47	TBALDC02	3.8	Unknown			83
5.82	TBALDC01	4.2	D-Limonene	C10H16	5989-27-5	97
5.83	TBALDC02	11.0	D-Limonene	C10H16	5989-27-5	96
6.68	TBALDC01	16.0	Methyl cinnamate	C6H6O3	61892-88-4	91
7.20	TBALDC02	0.87	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)	C10H18O	562-74-3	96
8.15	TBALDC02	1.3	.alpha.- Fenchyl acetate	C12H20O2	4057-31-2	99
9.38	TBALDC01	34.0	trans-Caryophyllene	C15H24	87-44-5	99
9.38	TBALDC02	11.0	trans-Caryophyllene	C15H24	87-44-5	99
9.64	TBALDC01	6.3	.beta.-Selinene	C15H24	17066-67-0	98
			.alpha.-Caryophyllene	C15H24	6753-98-6	97
9.65	TBALDC02	2.0	.beta.-Selinene	C15H24	17066-67-0	98
			.alpha.-Caryophyllene	C15H24	6753-98-6	97

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
10.33	TBALDC01	6.2	2-Butanone, 4-(4-hydroxyphenyl)	C10H12O2	5471-51-2	95
10.33	TBALDC02	1.7	2-Butanone, 4-(4-hydroxyphenyl)	C10H12O2	5471-51-2	97
10.40	TBALDC01	3.8	Unknown			83
10.72	TBALDC01	20.0	Unknown			58
10.72	TBALDC02	5.3	Caryophyllene oxide	C15H24O	1139-30-6	87
11.77	TBALDC01	12.0	Unknown			38
11.77	TBALDC02	8.7	Unknown			55
12.62	TBALDC02	8.2	Unknown			46
13.45	TBALDC01	11.0	Sandaracopimaradiene	C20H32	1686-56-2	93
13.46	TBALDC02	19.0	Sandaracopimaradiene	C20H32	1686-56-2	89
13.99	TBALDC02	3.0	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-	C20H30	19407-28-4	99
15.56	TBALDC01	1.4	Unknown			83
15.58	TBALDC02	1.7	Unknown			58
16.17	TBALDC01	1.6	Unknown			86
16.17	TBALDC02	1.1	Unknown			86
17.15	TBALDC02	0.56	1,3,7,9-Tetramethoxydibenzofuran-4-carbaldehyde	C17H16O6	85950-00-1	90
18.69	TBALDC01	0.60	Unknown			46
21.94	TBALDC02	0.66	Stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6	96

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Eastern Red Cedar Roots

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
4.96	REASTERNC01	1.8	Cyclohexene, 1-methyl-4-(1-methylethenyl)-	C10H16	5989-27-5	97
4.96	REASTERNC02	1.9	Cyclohexene, 1-methyl-4-(1-methylethenyl)-	C10H16	5989-27-5	97
8.98	REASTERNC01	0.67	Unknown			80
8.99	REASTERNC02	1.6	Unknown			59
9.13	REASTERNC01	1.0	1,4-Methano-1H-indene, octahydro-4-methyl-8-methylene-7-(1-methylethyl)	C15H24	3650-28-0	99
9.13	REASTERNC02	0.97	Unknown			72
9.25	REASTERNC01	1.7	Unknown			62
9.26	REASTERNC02	2.2	Unknown			52
9.32	REASTERNC02	2.6	Junipene	C15H24	475-20-7	99
9.37	REASTERNC02	1.1	trans-Caryophyllene	C15H24	87-44-5	99
9.48	REASTERNC02	0.67	Widdrene or Thujopsene	C15H24	470-40-6	99
9.63	REASTERNC02	0.54	1H-Benzocycloheptene, 2,4a,5,6,7,8,9,9a-octahydro-	C15H24	3853-83-6	95
9.68	REASTERNC02	1.2	Bicyclo[4.4.0]dec-1-en, 2-isopropyl-5-methyl-9-methylene	C15H24	0-00-0	86
9.78	REASTERNC02	3.0	Unknown			78
9.84	REASTERNC02	2.3	Unknown			78
9.99	REASTERNC01	2.2	Calarene	C15H24	17334-55-3	95
9.99	REASTERNC01	2.2	Valencene	C15H24	4630-07-3	95
9.99	REASTERNC02	2.3	Valencene	C15H24	4630-07-3	96
10.20	REASTERNC01	1.4	Bicyclo[4.4.0]dec-1-en, 2-isopropyl-5-methyl-9-methylene	C15H24	0-00-0	90
10.19	REASTERNC02	1.4	Bicyclo[4.4.0]dec-1-en, 2-isopropyl-5-methyl-9-methylene	C15H24	0-00-0	90
10.24	REASTERNC02	0.59	Unknown			49

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
10.89	REASTERNC01	0.69	Cedrol	C15H26O	77-53-2	93
10.90	REASTERNC02	1.2	8.beta. H-Cedran-8-ol	C15H26O	0-00-0	94
11.09	REASTERNC01	28.0	Unknown			50
11.09	REASTERNC02	32.0	Unknown			50
11.21	REASTERNC01	7.7	Unknown			47
11.21	REASTERNC02	5.7	Unknown			60
11.30	REASTERNC01	5.2	Unknown			49
11.36	REASTERNC01	2.9	Unknown			44
13.99	REASTERNC01	6.6	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-	C20H30	19407-28-4	98
14.00	REASTERNC02	9.7	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimethyl-7-(1-methylethyl)			99
14.86	REASTERNC01	13.0	Unknown			27
14.85	REASTERNC02	4.4	Unknown			25
15.33	REASTERNC01	28.0	Totarol	C20H30O	511-15-9	97
15.33	REASTERNC02	11.0	Totarol	C20H30O	511-15-9	98
15.50	REASTERNC01	81.0	Totarol	C20H30O	511-15-9	96
15.51	REASTERNC02	39.0	Totarol	C20H30O	511-15-9	96
16.29	REASTERNC01	6.4	Totarolone	C20H28O2	6755-93-7	86
16.29	REASTERNC02	5.1	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1,1,4a-trimethyl-7-(1-methylethyl)	C21H32O	10064-26-3	89
16.57	REASTERNC01	13.0	Unknown			55
16.91	REASTERNC01	5.6	Unknown			78
16.90	REASTERNC02	3.6	Podocarpa-8,11,13-teiene-3.alpha.,13-diol,14-iospropyl-	C20H30O2	18325-87-6	90
17.29	REASTERNC01	5.8	Unknown			70
21.89	REASTERNC01	11.0	Stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6	91
21.90	REASTERNC02	6.8	Stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6	96

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Eastern Red Cedar Tops

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
4.89	TEASTERNC01	0.56	Thujene	C10H16	2867-05-2	94
4.89	TEASTERNC02	0.71	Thujene	C10H16	2867-05-2	94
4.99	TEASTERNC01	0.83	Cyclohexene, 1-methyl-4-(1-methylethenyl)	C10H16	5989-27-5	97
4.97	TEASTERNC02	0.97	Cyclohexene, 1-methyl-4-(1-methylethenyl)	C10H16	5989-27-5	96
5.48	TEASTERNC01	1.2	.beta.-Myrcene	C10H16	123-35-3	91
5.86	TEASTERNC01	0.60	dl-Limonene	C10H16	138-86-3	95
5.85	TEASTERNC02	0.64	dl-Limonene	C10H16	138-86-3	96
7.61	TEASTERNC01	6.2	6-Octen-1-ol, 3,7-dimethyl	C10H20O	1117-61-9	98
7.59	TEASTERNC02	2.3	6-Octen-1-ol, 3,7-dimethyl	C10H20O	1117-61-9	98
7.82	TEASTERNC02	2.6	Unknown			80
9.07	TEASTERNC02	0.62	2,4-Diisopropenyl-1-methyl-1-vinyl-cyclohexane	C15H24	0-00-0	96
9.41	TEASTERNC01	1.6	trans-Caryophyllene	C15H24	87-44-5	99
9.41	TEASTERNC02	2.6	trans-Caryophyllene	C15H24	87-44-5	95
9.66	TEASTERNC02	0.64	.beta.-Selinene	C15H24	17066-67-0	98
9.79	TEASTERNC02	0.91	(-)-AR-Curcumene	C15H22	4176-06-1	95
10.01	TEASTERNC02	1.3	Unknown			64
10.12	TEASTERNC02	0.98	.gamma.-Cadinene	C15H24	39029-41-9	97
10.16	TEASTERNC02	1.1	.delta.-Cadinene	C15H24	483-76-1	98
10.43	TEASTERNC01	0.79	Hedycaryol	C15H26O	21657-90-9	80
10.43	TEASTERNC02	2.3	Hedycaryol	C15H26O	21657-90-9	87
10.50	TEASTERNC02	0.53	Germacrene B	C15H24	15423-57-1	92
10.73	TEASTERNC01	4.2	Unknown			72
10.73	TEASTERNC02	6.2	Unknown			50
11.53	TEASTERNC02	1.3	Unknown			43
11.80	TEASTERNC01	3.1	Unknown			46

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
11.87	TEASTERNC01	4.4	Unknown			58
11.86	TEASTERNC02	3.3	Unknown			50
12.32	TEASTERNC02	1.5	Unknown			55
12.46	TEASTERNC02	2.6	Unknown			25
14.22	TEASTERNC01	4.8	Unknown			64
14.19	TEASTERNC02	2.5	Unknown			52
14.88	TEASTERNC01	0.84	Unknown			38
14.97	TEASTERNC02	3.9	Unknown			43
15.00	TEASTERNC01	1.6	Unknown			50
15.08	TEASTERNC01	0.75	Unknown			38
15.14	TEASTERNC01	0.92	Unknown			83
15.38	TEASTERNC01	1.2	Unknown			86
15.51	TEASTERNC01	2.7	Unknown			27
15.48	TEASTERNC02	6.6	Unknown			38
15.58	TEASTERNC01	0.92	Unknown			80
15.63	TEASTERNC01	1.7	4,4-Dimethyl-13.alpha.-androst-5-ene	C21H34	73495-94-0	90
15.68	TEASTERNC01	1.1	Unknown			38
15.81	TEASTERNC02	4.3	Unknown			27
15.93	TEASTERNC01	1.4	Unknown			50
15.88	TEASTERNC02	2.2	Unknown			70
16.07	TEASTERNC01	3.4	6.Beta.-Hydroxyester-4-ene-3,17-dione	C18H24O3	5949-49-5	90
16.03	TEASTERNC02	9.2	Unknown			78
16.83	TEASTERNC01	1.0	Hinokione	C20H28O2	472-37-7	96
17.25	TEASTERNC01	0.59	9(1H)-Phenanthrenone, 2,3,4,4a,10,10a-hexahydro-6-hydroxy-1,1,4a-trimethyl-7	C20H28O2	511-05-7	96
21.96	TEASTERNC01	0.91	24.XI.-Ethylcholest-5-en-3.beta.-ol	C29H50O	19044-06-5	90
21.90	TEASTERNC02	2.2	Stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6	91

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Spruce Pine Roots

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
4.85	RSPRUPINE01	3.3	Tricyclo[2.2.1.02,6] heptane, 1,7,7-trimethyl-	C10H16	508-32-7	96
4.86	RSPRUPINE02	2.2	Tricyclo[2.2.1.02,6] heptane, 1,7,7-trimethyl-	C10H16	508-32-7	96
4.98	RSPRUPINE01	100	.alpha. -Pinene, (-) -	C10H16	80-56-8	96
5.01	RSPRUPINE02	38	.alpha. -Pinene, (-) -	C10H16	80-56-8	96
5.11	RSPRUPINE01	34	Camphene	C10H16	79-92-5	98
5.13	RSPRUPINE02	13	Camphene	C10H16	79-92-5	98
5.39	RSPRUPINE01	120	.beta. -Pinene	C10H16	127-91-3	97
5.43	RSPRUPINE01	10	.beta. -Myrcene	C10H16	123-35-3	94
5.44	RSPRUPINE02	43	2- .beta. -Pinene	C10H16	127-91-3	95
5.46	RSPRUPINE01	16	Unknown			83
5.48	RSPRUPINE02	2.8	Unknown			83
5.82	RSPRUPINE01	34	dl-Limonene	C10H16	138-86-3	96
5.84	RSPRUPINE02	15	dl-Limonene	C10H16	138-86-3	94
9.10	RSPRUPINE02	2.5	Unknown			38
9.36	RSPRUPINE01	2.9	Trans-caryophyllene	C15H24	87-44-5	98
9.35	RSPRUPINE02	2.5	Trans-caryophyllene	C15H24	87-44-5	99
9.60	RSPRUPINE01	4.0	1-Decene	C10H20	872-05-9	94
9.60	RSPRUPINE02	2.2	1-Decene	C10H20	872-05-9	95
11.76	RSPRUPINE02	2.5	Unknown			50
13.63	RSPRUPINE01	4.0	Unknown			70
13.63	RSPRUPINE02	3.7	Unknown			83
14.73	RSPRUPINE02	2.8	Unknown			59
15.05	RSPRUPINE01	4.6	Unknown			25
15.05	RSPRUPINE02	4.5	Unknown			30
15.14	RSPRUPINE01	4.2	Unknown			38
15.13	RSPRUPINE02	4.0	Unknown			38
15.22	RSPRUPINE02	2.5	(1R, 3S) - Cembra-4,7,11,15-tetraen-3-ol	C20H32O	79859-57-7	92
15.38	RSPRUPINE02	4.7	Unknown			47

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
15.48	RSPRUPINE01	6.8	Methyl levopimarate	C21H32O2	3513-69-7	93
15.48	RSPRUPINE02	7.5	Methyl levopimarate	C21H32O2	3513-69-7	93
15.54	RSPRUPINE01	5.5	Unknown			56
15.54	RSPRUPINE02	5.9	Unknown			72
15.63	RSPRUPINE02	2.4	1-Phenanthrenecarboxylic acid	C20H28O2	1740-19-8	98
15.79	RSPRUPINE02	5.2	Unknown			83
15.90	RSPRUPINE02	3.9	Methyl abietate	C21H32O2	127-25-3	91
21.89	RSPRUPINE02	4.0	Unknown			50

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Spruce Pine Tops

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
3.68	TSPRUPINE01	1.3	Hexanal	C6H12O	66-25-1	90
3.68	TSPRUPINE02	2.0	Hexanal	C6H12O	66-25-1	90
4.19	TSPRUPINE01	1.2	2-Hexenal	C6H10O	505-57-7	97
4.18	TSPRUPINE02	1.2	2-Hexenal	C6H10O	505-57-7	97
4.87	TSPRUPINE01	4.3	Tricyclo[2.2.1.02,6]heptane, 1,7,7-trimethyl	C10H16	508-32-7	96
4.87	TSPRUPINE02	3.8	Tricyclo[2.2.1.02,6]heptane, 1,7,7-trimethyl	C10H16	508-32-7	96
5.06	TSPRUPINE01	97	.alpha. -Pinene, (-) -	C10H16	80-56-8	96
5.04	TSPRUPINE02	120	.alpha. -Pinene, (-) -	C10H16	80-56-8	96
5.15	TSPRUPINE01	18	Camphene	C10H16	79-92-5	98
5.14	TSPRUPINE02	18	Camphene	C10H16	79-92-5	98
5.45	TSPRUPINE01	66	2-.beta. -Pinene	C10H16	127-91-3	96
5.42	TSPRUPINE02	75	2-.beta. -Pinene	C10H16	127-91-3	95
5.50	TSPRUPINE01	3.4	Unknown			83
5.61	TSPRUPINE01	0.9	.alpha. -Thujene	C10H16	2867-05-2	91
5.61	TSPRUPINE02	1.1	L-Phellandrene	C10H16	99-83-2	94
5.85	TSPRUPINE01	26	dl-Limonene	C10H16	138-86-3	91
5.85	TSPRUPINE02	34	Tricyclene	C10H16	508-32-7	91
6.89	TSPRUPINE01	0.6	Unknown			46
7.78	TSPRUPINE01	0.8	Linalyl acetate	C12H20O2	115-95-7	91
8.48	TSPRUPINE01	0.6	Unknown			97
9.40	TSPRUPINE01	2.8	Transcaryophyllene	C15H24	87-44-5	99
9.41	TSPRUPINE02	4.5	Transcaryophyllene	C15H24	87-44-5	99
9.67	TSPRUPINE01	1.0	.beta. -Selinene	C15H24	17066-67-0	97
9.66	TSPRUPINE02	1.6	.beta. -Selinene	C15H24	17066-67-0	98
14.74	TSPRUPINE01	0.9	Unknown			45
14.84	TSPRUPINE02	2.4	Unknown			49
15.05	TSPRUPINE02	2.3	Unknown			43
15.48	TSPRUPINE01	1.1	Methyl levopimarate	C21H32O2	3513-69-7	98

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
15.49	TSPRUPINE02	1.8	Unknown			47
15.91	TSPRUPINE01	1.4	1-Phenanethrenecarboxylic acid	C21H32O2	19402-34-7	90
15.90	TSPRUPINE02	2.1	Unknown			78
21.91	TSPRUPINE01	3.3	24.XI. -Ethylchlolest-5-en-3.beta-ol	C29H50O	19044-06-5	86
21.91	TSPRUPINE02	10	Unknown			78

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Water Oak Roots

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
3.57	RWOAK01	3.1	2,3-Butanediol	C4H10O2	513-85-9	87
5.46	RWOAK01	6.2	Unknown			83
5.46	RWOAK02	9.2	Unknown			83
9.28	RWOAK02	2.8	Unknown			72
9.60	RWOAK01	2.4	1-Decene	C12H24	872-05-9	94
9.60	RWOAK02	2.8	1-Decene	C12H24	872-05-9	95
15.29	RWOAK01	1.8	Androstan-17-one	C19H30O	963-74-6	94
21.90	RWOAK01	9.8	Unknown			64
21.89	RWOAK02	5.5	Unknown			43
22.63	RWOAK02	2.8	Unknown			50

Summary of Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 1 Water Oak Tops

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
3.60	TWOAK02	2.7	2,3-Butanediol	C4H10O2	513-85-9	91
3.66	TWOAK01	6.2	4-Pentenal, 2-methyl-	C6H10O	5187-71-3	90
3.67	TWOAK02	13.0	Unknown			60
3.95	TWOAK01	1.3	Unknown			72
3.96	TWOAK02	1.0	Unknown			59
4.11	TWOAK02	0.57	Unknown			68
4.17	TWOAK01	7.6	2-Hexenal	C6H10O	6728-26-3	95
4.19	TWOAK02	12.0	2-Hexenal	C6H10O	6728-26-3	97
5.03	TWOAK02	0.79	Unknown			45
5.15	TWOAK02	1.2	Unknown			47
5.47	TWOAK01	6.0	Unknown			83
5.47	TWOAK02	3.3	0-Chlorophenol-D4	C6HD4ClO	0-00-0	90
5.87	TWOAK02	1.0	Benzyl Alcohol	C7H8O	100-51-6	97
6.04	TWOAK01	1.2	Unknown			47
6.05	TWOAK02	2.4	Unknown			64
9.14	TWOAK01	1.1	Unknown			70
9.31	TWOAK01	7.4	Benzene ethanol, 4-hydroxy-	C8H10O2	501-94-0	91
9.29	TWOAK02	1.1	Unknown			64
9.60	TWOAK01	1.8	1-Decene	C12H24	872-05-9	93
9.60	TWOAK02	1.4	Cyclododecane	C12H24	294-62-2	97
11.78	TWOAK01	3.1	2-Propenoic acid	C10H10O3	3943-95-1	97
11.78	TWOAK02	1.1	2-Propenoic acid	C10H10O3	3943-97-3	97
21.91	TWOAK01	22.0	Stigmast-5-en-3-ol	C29H50O	83-47-6	91
21.91	TWOAK02	22.0	Unknown			81
22.17	TWOAK02	2.6	Unknown			38
22.30	TWOAK01	13.0	Unknown			83
22.30	TWOAK02	10.0	Unknown			68
22.66	TWOAK01	36.0	Unknown			76

Table Continued

Peak RT (min)	Sample ID	Estimated Concentration (mg/kg)	Chemical Name	Chemical Formula	CAS No.	Quality Factor
22.67	TWOAK02	5.6	Viminalol	C30H50O	638-95-9	93
22.77	TWOAK02	31.0	Unknown			83
23.08	TWOAK02	1.4	Unknown			43

Year 1 – Final Plant Tics

Please note that Spruce pine final TICs are not found in this appendix because the spruce pines were not sampled at the end of the first year study because of high mortality rates.

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 1 Black Willow Roots

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
100% COC	1BW3R	VOC	1.86	0.031	78	1-Propene, 2-methyl-	C4H8	115-11-7
	3BW3R	VOC	1.87	0.032	64	1-Propene, 2-methyl-	C4H8	115-11-7
	1BW3R	SVOC	8.06	1.6	40	Unknown	n/a	n/a
	1BW3R	SVOC	16.31	1.1	43	Unknown	n/a	n/a
	1BW3R	SVOC	19.30	1.3	47	Unknown	n/a	n/a
	1BW3R	SVOC	22.01	0.87	45	Unknown	n/a	n/a
	1BW3R	SVOC	22.08	1.9	32	Unknown	n/a	n/a
	1BW3R	SVOC	23.86	13	30	Unknown	n/a	n/a
	2BW3R	SVOC	8.06	2.1	38	Unknown	n/a	n/a
	2BW3R	SVOC	13.01	1.2	90	Decanoic acid, methyl ester	C11H2202	110-42-9
	2BW3R (BD-2)	SVOC	8.02	0.91	42	Unknown	n/a	n/a
	2BW3R (BD-2)	SVOC	12.95	1.1	93	Hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	2BW3R (BD-2)	SVOC	18.38	0.82	78	Unknown	n/a	n/a
	2BW3R (BD-2)	SVOC	18.43	0.88	46	Unknown	n/a	n/a
	2BW3R (BD-2)	SVOC	19.20	1.0	43	Unknown	n/a	n/a
2BW3R (BD-2)	SVOC	22.19	1.3	42	Unknown	n/a	n/a	

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	3BW3R	SVOC	5.85	1.2	96	Benzaldehyde, 4-hydroxy-	C7H6O2	123-08-0
	3BW3R	SVOC	8.05	0.98	38	Unknown	n/a	n/a
	3BW3R	SVOC	8.79	0.89	37	Unknown	n/a	n/a
	3BW3R	SVOC	13.00	0.81	83	Tridecanoic acid, methyl ester	C14H28O2	1731-88-0
	3BW3R	SVOC	17.33	1.1	59	Unknown	n/a	n/a
	3BW3R	SVOC	18.52	1.4	43	Unknown	n/a	n/a
	4BW3R	SVOC	5.85	0.82	87	Benzene-acetaldehyde	C8H8O	122-78-1
	4BW3R	SVOC	8.07	2.2	40	Unknown	n/a	n/a
	4BW3R	SVOC	17.34	0.87	25	Unknown	n/a	n/a
	4BW3R	SVOC	19.31	1.1	51	Unknown	n/a	n/a
	4BW3R	SVOC	23.42	2.9	64	Unknown	n/a	n/a
67%	5BW4R	VOC	NONE					
COC	2BW4R	VOC	1.89	0.01	72	Unknown	n/a	n/a
	4BW4R	VOC	1.85	0.0	59	Unknown	n/a	n/a
	3BW4R	VOC	NONE					
	4BW4R	SVOC	4.87	0.82	64	Unknown	n/a	n/a
	4BW4R	SVOC	15.75	1.5	22	Unknown	n/a	n/a
	4BW4R	SVOC	16.32	1.2	72	Unknown	n/a	n/a
	4BW4R	SVOC	18.53	1	50	Unknown	n/a	n/a
	4BW4R	SVOC	17.35	2.1				
	3BW4R	SVOC	9.89	0.83	64	Unknown	n/a	n/a
	5BW4R	SVOC	13	1.4	83	Pentadecanoic acid, methyl ester	C16H32O2	7132-64-1
	5BW4R	SVOC	22.31	2.3	83	2-(4`-Nitro-2`-thienyl) pyrimidine	C8H5N3O2S	57059-15-1
33%	2BW4R	SVOC	NONE					
COC	2BW6R	VOC	NONE					
	IBW6R	VOC	14.35	0.013	81	3-octanone	C8H16O	106-68-3

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	5BW5R	VOC	NONE					
	4BW6R	VOC	NONE					
	2BW6R	SVOC	20.14	0.81	53	Unknown	n/a	n/a
	2BW6R	SVOC	15.04	5.5	60	Unknown	n/a	n/a
	2BW6R	SVOC	15.95	20	53	Unknown	n/a	n/a
	2BW6R	SVOC	21.77	0.95	50	Unknown	n/a	n/a
	2BW6R	SVOC	21.98	0.96	42	Unknown	n/a	n/a
	2BW6R	SVOC	23.45	1	51	Unknown	n/a	n/a
	2BW6R	SVOC	24.06	0.93	47	Unknown	n/a	n/a
	IBW6R	SVOC	9.55	4.9	59	Unknown	n/a	n/a
	IBW6R	SVOC	12.96	0.99	76	Hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	IBW6R	SVOC	15.06	1	58	Unknown	n/a	n/a
	IBW6R	SVOC	8.14	0.93	64	Unknown	n/a	n/a
	5BW5R	SVOC	19.31	0.94	50	Unknown	n/a	n/a
	5BW5R	SVOC	21.8	0.91	46	Unknown	n/a	n/a
	5BW5R	SVOC	6.1	4.7	72	Unknown	n/a	n/a
	5BW5R	SVOC	16.84	5.3	47	Unknown	n/a	n/a
	5BW5R	SVOC	19.46	5.8	55	Unknown	n/a	n/a
	4BW6R	SVOC	6.8	2.2	78	4-Pyridine-carboxamide, N-hydroxy-	C6H6N2O2	4427-22-9
	4BW6R	SVOC	18.72	0.8	46	Unknown	n/a	n/a
	4BW6R	SVOC	19.31	1.3	46	Unknown	n/a	n/a
	4BW6R	SVOC	5.85	1.5	72	Unknown	n/a	n/a

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 1 Black Willow Tops

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
100% COC	1BW3T	VOC	n.a.					
	2BW3T	VOC	n.a.					
	2BW3T BD2-T	VOC	n.a.					
	3BW3T	VOC	n.a.					
	4BW3T	VOC	n.a.					
	1BW3T	SVOC	14.06	2.2	93	9,12-Octadecadienoic acid, methyl ester, (E,E)-	C19H34O2	2566-97-4
	1BW3T	SVOC	14.17	2.7	72	phytol	C20H4O0	150-86-7
	1BW3T	SVOC	15.14	7.4	47	Unknown	n/a	n/a
	1BW3T	SVOC	16.26	3.6	83	17-Pentatriacontene	C35H70	6971-40-0
	1BW3T	SVOC	18.72	4.4	53	Unknown	n/a	n/a
	2BW3T	SVOC	7.77	1.5	80	Nerol	C10H18O	106-25-2
	2BW3T	SVOC	9.03	0.87	27	Unknown	n/a	n/a
	2BW3T BD2-T	SVOC	13.54	3	46	Unknown	n/a	n/a
	2BW3T BD2-T	SVOC	15.42	22	37	Unknown	n/a	n/a
	2BW3T BD2-T	SVOC	19.08	3.9	38	Unknown	n/a	n/a
	3BW3T	SVOC	14.70	2.2	45	Unknown	n/a	n/a
	3BW3T	SVOC	16.25	2.1	35	Unknown	n/a	n/a
	4BW3T	SVOC	7.78	1.3	72	2,6-Octadien-1-ol, 3,7-dimethyl-, (Z)-	C10H18O	106-25-2
	4BW3T	SVOC	13.55	1.6	83	2-Isopropyl-6,6-dimethyl-1-oxaspiro[2.5]octane-4,8-dione	C12H18O3	83814-11-3

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	4BW3T	SVOC	14.05	1.5	83	9-Octadecynoic acid, methyl ester	C19H34O2	1120-32-7
67% COC	4BW4T	VOC	3.32	0.005	91	Dimethyl sulfide	C2H6S	75-18-3
	3BW4T	VOC	3.34	0.005	91	Dimethyl sulfide	C2H6S	75-18-3
	2BW4T	VOC	3.34	0.005	90	Dimethyl sulfide	C2H6S	75-18-3
	5BW4T	VOC	NONE					
	4BW4T	SVOC	5.14	2	91	Bicyclo[3.1.0] hexane, 4-methylene-1-(1-methylethyl)-	C10H16	3387-41-5
	4BW4T	SVOC	5.78	5	86	Benzenemethanol	C7H8O	100-51-6
	4BW4T	SVOC	5.88	2	94	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8
	4BW4T	SVOC	6.61	8.7	91	Benzeneethanol	C8H10O	60-12-8
	4BW4T	SVOC	8.87	1.8	72	Unknown	n/a	n/a
	4BW4T	SVOC	9.47	2	64	Unknown	n/a	n/a
	4BW4T	SVOC	10.62	1.7	38	Unknown	n/a	n/a
	4BW4T	SVOC	13.34	7.7	91	Hexadecanoic acid	C16H32O2	57-10-3
	4BW4T	SVOC	14.85	2.9	43	Unknown	n/a	n/a
	4BW4T	SVOC	18.15	2.9	43	Unknown	n/a	n/a
	4BW4T	SVOC	19.64	9.2	83	16-Octadecenal	C18H34O	56554-87-1
	3BW4T	SVOC	6.6	9.2	91	Phenylethyl alcohol	C8H10O	60-12-8
	3BW4T	SVOC	8.96	1	90	4-methoxyphenethyl alcohol	C9H12O2	702-23-8
	3BW4T	SVOC	9.45	1.4	64	Unknown	n/a	n/a
	3BW4T	SVOC	13.33	6	91	Hexadecanoic acid	C16H32O2	57-10-3
	3BW4T	SVOC	14.4	2.7	91	9,12-octadecadienoic acid (Z,Z)-	C18H32O2	60-33-3
	3BW4T	SVOC	15.67	1.4	59	Unknown	n/a	n/a
	3BW4T	SVOC	18.13	1.6	59	Unknown	n/a	n/a

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	3BW4T	SVOC	19.61	3.8	90	Hexadecanal	C16H32O	629-80-1
	3BW4T	SVOC	20.04	3.6	86	Heptadecane	C17H36	629-78-7
	3BW4T	SVOC	20.54	4.5	53	Unknown	n/a	n/a
	3BW4T	SVOC	21.73	20	72	Unknown	n/a	n/a
	3BW4T	SVOC	24.43	7.6	47	Unknown	n/a	n/a
	5BW4T	SVOC	13.31	6.6	92	Hexadecanoic acid	C16H32O2	57-10-3
	5BW4T	SVOC	14.39	2.3	58	Unknown	n/a	n/a
	5BW4T	SVOC	14.82	3.4	28	Unknown	n/a	n/a
	5BW4T	SVOC	19.61	6.6	78	Tetradecanal	C14H28O	124-25-4
	5BW4T	SVOC	20.04	3	76	Octadecane	C18H38	593-45-3
	5BW4T	SVOC	20.31	3	47	Unknown	n/a	n/a
	5BW4T	SVOC	20.54	5.9	80	Pentadecanal	C15H30O	11/9/2765
	5BW4T	SVOC	21.73	3.2	72	Unknown	n/a	n/a
	5BW4T	SVOC	24.42	11	43	Unknown	n/a	n/a
	2BW4T	SVOC	6.23	90	80	1,2- cyclohexanediol, trans-	C6H12O2	1460-57-7
	2BW4T	SVOC	6.77	1.8	72	Unknown	n/a	n/a
	2BW4T	SVOC	7.69	1.8	94	2-Coumaranone	C8H6O2	553-86-6
	2BW4T	SVOC	12.43	1.5	27	Unknown	n/a	n/a
	2BW4T	SVOC	13.48	1.4	42	Unknown	n/a	n/a
	2BW4T	SVOC	14.06	1.5	83	(r)-(-)-14- methyl -8-hexadecyn-1-ol	C17H32O	64566-18-3
	2BW4T	SVOC	15.61	2.3	64	Unknown	n/a	n/a
33% COC	2BW6T	VOC	3.36	0.01	97	Dimethyl sulfide	C2H6S	75-18-3
	1BW6T	VOC	NONE					
	5BW5T	VOC	3.35	0.006	91	Dimethyl sulfide	C2H6S	75-18-3
	4BW6T	VOC	2.82	0.006	74	Unknown	n/a	n/a
	4BW6T	VOC	3.32	0.009	95	Dimethyl sulfide	C2H6S	75-18-3
	4BW6T	VOC	14.36	0.005	72	Unknown	n/a	n/a
	2BW6T	SVOC	6.78	1.9	72	Unknown	n/a	n/a

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	2BW6T	SVOC	9.15	1.8	53	Unknown	n/a	n/a
	2BW6T	SVOC	12.43	1.6	42	Unknown	n/a	n/a
	2BW6T	SVOC	14.06	1.8	58	Unknown	n/a	n/a
	2BW6T	SVOC	16.78	4.1	25	Unknown	n/a	n/a
	2BW6T	SVOC	24.18	3.8	53	Unknown	n/a	n/a
	1BW6T	SVOC	7.78	1.5	93	trans-geraniol	C10H18O	106-24-1
	1BW6T	SVOC	15.61	4	47	Unknown	n/a	n/a
	1BW6T	SVOC	16.77	3.7	38	Unknown	n/a	n/a
	5BW5T	SVOC	6.77	1.9	72	Unknown	n/a	n/a
	5BW5T	SVOC	12.45	2.1	25	Unknown	n/a	n/a
	5BW5T	SVOC	14.05	1.4	86	(r)-(-)-14- methyl -8-hexadecyn-1-ol	C17H32O	64566-18-3
	5BW5T	SVOC	16.26	2	52	Unknown	n/a	n/a
	4BW6T	SVOC	8.38	26	94	2-propen-1-ol,3-phenyl-	C9H10O	104-54-1
	4BW6T	SVOC	16.26	2.6	58	Unknown	n/a	n/a
	4BW6T	SVOC	24.18	6.8	40	Unknown	n/a	n/a

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples –Year 1 Eastern Red Cedar Roots

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
100% COC	4ERC3R	VOC	1.98	.420	90	Acetaldehyde	C2H4O	75-07-0
	4ERC3R	VOC	13.91	.116	97	Bicyclo {3.1.0} hexane,4-methyl truncated	C10H16	3387-41-5
	4ERC3R	VOC	15.33	.230	97	Cyclohexene, 1-methyl-4 (1-meth truncated	C10H16	586-62-9
	3ERC3R	VOC	15.11	.408	50	unknown	N/A	N/A
	3ERC3R	VOC	16	.266	55	unknown	N/A	N/A
	5ERC3R	VOC	2.01	.550	90	Acetaldehyde	C2H4O	75-07-0
	5ERC3R	VOC	15.5	0.136	97	Spiro [5.5] undec-2-ene, 3,7,7-trimethy truncated	C15H24	18431-82-8
	5ERC3R	VOC	15.98	.259	96	1H-Benzenocycloheptene , 2,4a, 5, 6,truncated	C15H24	1461-03-6
	5ERC3R	VOC	16.18	.169	93	(+) - 2- carene	C15H22	16982-00-6
	1ERC3R	VOC	15.33	.149	98	Benzene, 1- methyl -4- (1,2,2- trimet truncated	C10H16	0-00-0
	1ERC3R	VOC	15.96	.145	92	1H-Benzenocycloheptene , 2,4a, truncated	C15H24	1461-03-6
	4ERC3R	SVOC	7.73	1.900	91	2-Isopropyl -1-methoxy-4- methylbenzene	C11H16O	0-00-0
	4ERC3R	SVOC	8.28	6.000	90	phenol, 3- (1-methethyl)-	C9H12O	618-45-1
	4ERC3R	SVOC	8.79	2.400	98	tricyclo [5.4.0.02,8] undec -9-ene, truncated	C15H12	

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	4ERC3R	SVOC	8.94	.830	96	ylangene	C15H24	14912-44-8
	4ERC3R	SVOC	9.68	1.700	76	Bicyclo [2.2.1] heptane,2,2 - dimet truncated	C10H16	
	4ERC3R	SVOC	10.74	.860	64	unknown	N/A	N/A
	4ERC3R	SVOC	12.39	8.800	70	unknown	N/A	N/A
	4ERC3R	SVOC	14.98	.820	55	unknown	N/A	N/A
	4ERC3R	SVOC	16.78	1.200	90	3,20 - dimethyl -a-nor-3 (5) - Pregnene	C22H36	62008-73-5
	4ERC3R	SVOC	16.83	1.600	99	Hinokione	C20H28O2	472-37-7
	3ERC3R	SVOC	10.76	.890	86	1,3,6 - heptatriene ,2,5,6 -trimethyl-	C10H16	42123-66-0
	3ERC3R	SVOC	11.7	7.600	50	unknown	N/A	N/A
	3ERC3R	SVOC	12.39	6.000	38	unknown	N/A	N/A
	5ERC3R	SVOC	13.06	5.200	32	unknown	N/A	N/A
	5ERC3R	SVOC	15.62	13.000	98	Totarol	C20H30O	511-15-9
	1ERC3R	SVOC	9.37	4.100	84	1-H- Cycloprop [e]azulene, deca truncated	C15H24	489-39-4
	1ERC3R	SVOC	15.03	9.800	49	unknown	N/A	N/A

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 1 Eastern Red Cedar Tops

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
100% COC	1ERC3T	VOC	14.73	.250	91	.beta. - Phellandrene	C10H16	555-10-2
	4ERC3T	VOC	NONE					
	5ERC3T	VOC	NONE					
	3ERC3T	VOC	NONE					
	1ERC3T	SVOC	6.5	2.400	64	unknown	n/a	n/a
	1ERC3T	SVOC	7.21	1.800	94	3-Cyclohexen -1-10-4- methyl-1-1 truncated	C10H18O	562-74-3
	1ERC3T	SVOC	9.79	1.200	94	Benzene, 1-(1,5 - dimethyl -4-hexe truncated	C15H22	644-30-4
	1ERC3T	SVOC	10.12	1.200	96	.gamma. -Cadinene	C15H24	39029-41-9
	1ERC3T	SVOC	10.16	1.300	96	naphthalene, 1,2,3,5,6,8a - hexahydro truncated	C15H24	483-76-1
	4ERC3T	SVOC	7.2	1.800	22	unknown	n/a	n/a
	4ERC3T	SVOC	9.22	1.200	96	(15,65)- 1,7,7- trimethyl-2,3 - dimethylid truncated	C15H24	58795-27-0
	4ERC3T	SVOC	9.77	3.200	93	Benzene, 1- (1,5 - dimethyl -4-hexenyl) truncated	C15H22	644-30-4
	4ERC3T	SVOC	11	1.600	16	unknown	n/a	n/a
	5ERC3T	SVOC	7.19	2.400	89	3-cyclohexen-1-ol, 4-methyl-1-(1-methle truncated	C10H18O	562-74-3
	5ERC3T	SVOC	10.1	1.800	96	.gamma.- Cadinene	C15H24	39029-41-9
	3ERC3T	SVOC	7.21	1.500	81	Benzenemethanol, 4- (1-methylethyl)-	C10H14O	536-60-7

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	3ERC3T	SVOC	7.73	1.000	91	2-isopropyl-1-methoxy -4-methylbenzene	C11H16O	0-00-0
	3ERC3T	SVOC	8.7	.930	99	.alpha.- cubene	C15H24	170699-14-8
	3ERC3T	SVOC	9.22	2	94	.beta. - Selinene	C15H24	17066-67-0
	3ERC3T	SVOC	9.78	1.400	56	unknown	n/a	n/a
	3ERC3T	SVOC	10.08	2.200	95	1,2,2 - trimethyl -1-(P-tolyl)-Cyclopentane	C15H22	16982-00-6
	3ERC3T	SVOC	10.29	2.5	91	.beta. - Himachalene	C15H24	1461-03-6
	3ERC3T	SVOC	11.39	2.000	78	1H- cycloprop [e] azulene, decahydro truncated	C15H24	25246-27-9
	3ERC3T	SVOC	11.56	1.600	50	unknown	n/a	n/a
	3ERC3T	SVOC	12.49	1.200	25	unknown	n/a	n/a

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 1 Bald Cypress Roots

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
100% COC	BD1	VOC	14.36	0.026	58	unknown	n/a	n/a
	5BC3R	VOC	3.82	0.029	91	methylene chloride	CH2Cl	75-09-2
	3BC3R	VOC	14.35	0.043	74	unknown	n/a	n/a
	4BC3R	VOC	NONE					
	2BC3R	VOC	3.83	0.035	97	methylene chloride	CH2Cl	75-09-2
	2BC3R	VOC	2.86	0.031	74	unknown	n/a	n/a
	BD1	SVOC	5.19	2.7	78	Ethanol,2,2'-oxybis	C4H10O3	111-46-6
	5BC3R	SVOC	6.55	1.2	86	D-fenchylalcohol	C10H18O	1632-73-1
	5BC3R	SVOC	11.87	2.6	52	unknown	n/a	n/a
	5BC3R	SVOC	14.06	1.3	60	unknown	n/a	n/a
	5BC3R	SVOC	14.38	7.8	64	unknown	n/a	n/a
	5BC3R	SVOC	15.06	0.82	35	unknown	n/a	n/a
	5BC3R	SVOC	15.21	1.6	43	unknown	n/a	n/a
	5BC3R	SVOC	15.41	2	58	unknown	n/a	n/a
	5BC3R	SVOC	15.83	1.6	90	2-(4'methoxyphenyl)-N-methylaniline	C14H15NO	73006-82-3
	5BC3R	SVOC	16.03	1.1	93	hinokione	C20H28O2	472-37-7
	5BC3R	SVOC	17.85	1.1	38	unknown	n/a	n/a
	3BC3R	SVOC	11.07	1.1	81	benzeacetic acid, 4-hydroxy-3-methoxy-	C9H10O4	306-08-1
	3BC3R	SVOC	13.97	0.89	99	9,12-octadecadienoic acid, truncated	C19H34O2	2566-97-4
	3BC3R	SVOC	15.53	18	25	unknown	n/a	n/a
	3BC3R	SVOC	16.9	0.98	25	unknown	n/a	n/a
	3BC3R	SVOC	20.95	0.97	90	(-) matairesinol	C20H22O6	580-72-3

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	4BC3R	SVOC	4.74	1.5	91	bicyclo[3.1.1] hept-2-ene,3,6,6-trimethyl-	C10H16	4889-83-2
	4BC3R	SVOC	12.7	1	47	unknown	n/a	n/a
	4BC3R	SVOC	15.21	1.3	59	unknown	n/a	n/a
	4BC3R	SVOC	16.71	1	91	2-hydroxy-3-methyl-4,6-dimethoxymethyl truncated	C18H20O6	74627-90-0
	2BC3R	SVOC	11.89	1.9	47	unknown	n/a	n/a
	2BC3R	SVOC	14.08	2.2	49	unknown	n/a	n/a
	2BC3R	SVOC	14.41	7.3	50	unknown	n/a	n/a
	2BC3R	SVOC	14.62	0.88	43	unknown	n/a	n/a
	2BC3R	SVOC	15.23	0.96	90	1-docosene	C22H44	1599-67-3
	2BC3R	SVOC	15.43	1.8	64	unknown	n/a	n/a
	2BC3R	SVOC	23.8	3.7	46	unknown	n/a	n/a
67% COC	2BC4R	VOC	3.81	0.031	95	methylene chloride	CH2Cl	75-09-2
	5BC4R	VOC	NONE					
	3BC4R	VOC	3.81	0.029	97	methylene chloride	CH2Cl	75-09-2
	3BC4R	VOC	14.02	0.027	91	.beta.-myrcene	C10H16	123-35-3
	1BC4R	VOC	2.84	0.03	74	unknown	n/a	n/a
	1BC4R	VOC	14.35	0.032	64	unknown	n/a	n/a
	2BC4R	SVOC	11.08	1.2	80	benzeacetic acid, 4-hydroxy-3 methoxy	C9H10O4	306-08-1
	2BC4R	SVOC	12.59	1.5	53	unknown	n/a	n/a
	2BC4R	SVOC	12.88	1.4	99	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	2BC4R	SVOC	13.97	4.6	91	1-napthalenepropanol,.alpha truncated	C20H34O	596-85-0
	2BC4R	SVOC	14.28	1.1	47	unknown	n/a	n/a
	2BC4R	SVOC	14.69	2.3	47	unknown	n/a	n/a
	2BC4R	SVOC	14.84	0.98	43	unknown	n/a	n/a

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	5BC4R	SVOC	10.34	1.2	91	d-nerolidol	C15H26O	142-50-7
	5BC4R	SVOC	11.02	1	86	calarene	C15H24	17334-55-3
	5BC4R	SVOC	11.09	1.3	87	benzeneacetic acid, 4-hydroxy-3-methoxy-	C9H10O4	306-08-1
	5BC4R	SVOC	11.2	1.2	96	eudesmol	C15H26O	51317-08-9
	5BC4R	SVOC	12.59	0.82	97	7-hexadecene, (2)-	C16H32	35507-09-6
	5BC4R	SVOC	12.87	0.84	97	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	5BC4R	SVOC	13.98	0.91	98	9,12-octadecadienoic acid, methyl ester, (E,E)-	C19H34O2	2566-97-4
	3BC4R	SVOC	10.34	1.5	91	1,6,10 - dodecadienoic -3-ol, 3,7,11-trimethyl - [s-(z)]-	C15H26O	142-50-7
	3BC4R	SVOC	11.02	1.5	94	(+)-.delta.-selinene	C15H24	28624-28-4
	3BC4R	SVOC	11.08	1.2	76	benzeneacetic acid, 4-hydroxy -3-methoxy-	C9H10O4	306-08-1
	3BC4R	SVOC	11.19	1.9	95	eudesmol	C15H26O	8/9/5137
	3BC4R	SVOC	11.65	1	38	unknown	n/a	n/a
	3BC4R	SVOC	12.59	1.2	55	unknown	n/a	n/a
	3BC4R	SVOC	13.98	1.4	83	o-tert-butyl phenoxy) benzoic acid	C17H18O3	69737-65-1
	1BC4R	SVOC	11.08	0.88	80	benzeneacetic acid, 4-hydroxy-3-methoxy-	C9H10O4	306-08-1
	1BC4R	SVOC	13.98	1.2	96	9,12-octadecadienoic acid, methyl ester (E,E)-	C19H34O2	2566-97-4
	1BC4R	SVOC	20.97	1.6	87	(-) matairesinol	C20H22O6	580-72-3

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
33% COC	1BC5R	VOC	NONE					
	5CY5R	VOC	NONE					
	4CY5R	VOC	NONE					
	5BC6R	VOC	15.17	0.025	95	cyclopropane,1-heptyl-2-methyl-	C11H22	74663-91-5
	5CY5R	SVOC	6.14	1.7	94	1,2-cyclohexanediol, trans-	C6H12O2	1460-57-7
	5CY5R	SVOC	6.14	1.7	94	cis-1,2-cyclohexanediol	C6H12O2	1792-81-0
	5CY5R	SVOC	7.38	0.86	64	unknown	n/a	n/a
	5CY5R	SVOC	7.98	1.2	94	salicyl alcohol	C7H8O2	90-01-7
	5CY5R	SVOC	12.91	0.8	98	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	5CY5R	SVOC	14.01	0.98	99	9,12-octadecadienoic acid, methyl ester	C19H34O2	2566-97-4
	5CY5R	SVOC	15.52	1.8	98	totarol	C20H30O	511-15-9
	4CY5R	SVOC	15.03	2.3	49	unknown	n/a	n/a
	5BC6R	SVOC	5.4	1	94	.beta.-myrcene	C10H16	123-35-3
	5BC6R	SVOC	8.12	1.2	98	endobornyl acetate	C12H20O2	76-49-3
	5BC6R	SVOC	10.34	0.84	91	1,6,10-dodecatrien -3-ol,3,7,11-trimethyl-,[S-(2)]-	C15H26O	142-50-7
	5BC6R	SVOC	11.02	1.4	83	1h-cyclopropa[a] naphthalene, truncated	C15H24	17334-55-3
	5BC6R	SVOC	11.08	1.7	83	benzeneacetic acid, 4-hydroxy -3- methoxy-	C9H10O4	306-08-1
	5BC6R	SVOC	11.19	1.4	60	unknown	n/a	n/a
	5BC6R	SVOC	12.59	1.4	53	unknown	n/a	n/a
	5BC6R	SVOC	12.81	0.83	95	9-hexadecenoic acid, methyl ester, (2)-	C17H32O2	1120-25-8
	5BC6R	SVOC	13.1	1.2	64	unknown	n/a	n/a

Table Continued

Sample ID	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	5BC6R	SVOC	13.97	2.7	46	unknown	n/a	n/a
	1BC5R	SVOC	11.07	1.4	83	benzeneacetic acid, 4-hydroxy -3- methoxy-	C9H10O4	306-08-1
	1BC5R	SVOC	12.87	1	98	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	1BC5R	SVOC	13.97	1.9	99	9,12-octadecadienoic acid, methyl ester, (E,E)-	C19H34O2	2566-97-4
	1BC5R	SVOC	14.67	1.5	78	ledane	C15H26	28580-43-0
	1BC5R	SVOC	16.91	0.98	38	unknown	n/a	n/a
	1BC5R	SVOC	17.18	2.2	96	9(1H)-phenanthrenone,2,3,4,4a truncated	C20H28O2	511-05-7

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 1 Bald Cypress Tops

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
100% COC	5BC3T	VOC	16.09	0.028	64	unknown	n/a	n/a
	4BC3T	VOC	3.08	0.096	96	methylene chloride	CH2CL2	75-09-2
	4BC3T	VOC	13.97	0.036	91	bicyclo[3-1-1] heptane, truncated	C10H16	18172-67-3
	4BC3T	VOC	13.97	0.036	87	.beta.-pinene	C10H16	127-91-3
	4BC3T	VOC	13.97	0.036	87	tricyclo[2.2.1.02,6]heptane truncated	C10H16	508-32-7
	3BC3T	VOC	12.99	0.071	96	tricyclo[2.2.1.02,6]heptan truncated	C10H16	508-32-7
	3BC3T	VOC	12.99	0.071	95	.alpha.-pinene	C10H16	80-56-8
	3BC3T	VOC	12.99	0.071	90	1,4-cyclohexadiene, 1-m truncated	C10H16	99-85-4
	3BC3T	VOC	13.88	0.039	91	bicyclo[3.1.1]heptane,6, truncated	C10H16	18172-67-3
	3BC3T	VOC	13.88	0.039	91	cyclohexene,4-methylen truncated	C10H16	99-84-3
	3BC3T	VOC	14.48	0.035	94	1,3-cyclohexadiene,1-met truncated	C10H16	99-86-5
	3BC3T	VOC	14.96	0.037	94	1,4-cyclohexadiene,1- truncated	C10H16	99-85-4
	2BC3T	VOC	3.34	0.041	94	dimethyl sulfide	C2H65	75-18-3
	2BC3T	VOC	3.81	0.081	97	methylene choride	CH2CL2	75-09-2
	2BC3T	VOC	13.98	0.194	97	.beta.-pinene	C10H16	127-91-3
	5BC3T	SVOC	6.6	0.89	96	BICYCLO[2.2.1]HEPT truncated	C10H18O	1632-73-1
	5BC3T	SVOC	8.73	0.84	96	benzaldehyde 4-hydroxy-	C7H6O2	123-08-0

Table Continued

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	5BC3T	SVOC	9.11	1	98	benzaldehyde 4-hydrox truncated	C8H8O3	121-33-5
	5BC3T	SVOC	12.87	1.2	97	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	5BC3T	SVOC	13.97	9.8	91	1-naphthalenepropanol truncated	C20H34O	596-85-0
	5BC3T	SVOC	14.68	1.2	70	unknown	n/a	n/a
	5BC3T	SVOC	16.18	1.2	94	1-nonadecanol	C19H40O	1454-84-8
	4BC3T	SVOC	12.7	0.88	43	unknown	n/a	n/a
	4BC3T	SVOC	13	1.1	94	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	4BC3T	SVOC	14.09	0.84	53	unknown	n/a	n/a
	4BC3T	SVOC	15.21	1.8	47	unknown	n/a	n/a
	3BC3T	SVOC	4.76	39	94	cyclohexene,1-methyl truncated	C10H16	5989-27-5
	3BC3T	SVOC	5.26	0.8	72	unknown	n/a	n/a
	3BC3T	SVOC	6.81	1.3	64	unknown	n/a	n/a
	3BC3T	SVOC	9.36	1	68	unknown	n/a	n/a
	3BC3T	SVOC	9.4	2	64	unknown	n/a	n/a
	3BC3T	SVOC	9.67	0.81	59	unknown	n/a	n/a
	3BC3T	SVOC	10.3	0.83	53	unknown	n/a	n/a
	3BC3T	SVOC	11.4	0.89	35	unknown	n/a	n/a
	3BC3T	SVOC	11.95	45	52	unknown	n/a	n/a
	3BC3T	SVOC	12.72	1.6	46	unknown	n/a	n/a
	3BC3T	SVOC	13.52	2	89	sandaracopimaradiene	C20H32	1686-56-2
	2BC3T	SVOC	4.74	12	94	bicyclo[3.1.1]hept-2-ene,3,6,6-trimethyl-	C10H16	4889-83-2
	2BC3T	SVOC	4.74	12	94	.alpha.-pinene	C10H16	80-56-8
	2BC3T	SVOC	12.7	1.1	55	unknown	n/a	n/a

Table Continued

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	2BC3T	SVOC	16.71	1.7	91	2-hydroxy-3-methyl-4,6 truncated	C18H20O6	74627-90-0
	2BC3T	SVOC	17.84	0.96	53	unknown	n/a	n/a
67% COC	2BC4T	VOC	3.78	.059	96	methylene chloride	CH2CL2	75-09-2
	2BC4T	VOC	16.09	.036	83	bicyclo [2.2.1] heptan-2-ol,1,3,3-trimethyl-	C10H18O	1632-73-1
	5BC4T	VOC	3.79	.116	97	methylene chloride	CH2CL2	75-09-2
	3BC4T	VOC	3.35	.051	94	dimethyl sulfide	C2H6S	75-18-3
	3BC4T	VOC	3.82	.038	94	methylene chloride	CH2CL2	75-09-2
	3BC4T	VOC	14.95	.034	95	1,4- cyclohexadiene truncated	C10H16	99-85-4
	3BC4T	VOC	16.09	.042	83	bicyclo [2.2.1] heptan-2 truncated	C10H18O	1632-73-1
	3BC4T	VOC	16.65	.049	83	isoborneol	C10H18O	124-76-5
	1BC4T	VOC	3.82	.054	94	methylene chloride	CH2CL2	75-09-2
	2BC4T	SVOC	6.6	0.99	96	bicyclo [2.2.1] heptan truncated	C10H18O	1632-73-1
	2BC4T	SVOC	9.26	0.96	96	phenol,3,4 -dimethoxy-	C8H10O3	2033-89-8
	2BC4T	SVOC	10.68	1.2	91	caryophyllene oxide	C15H24O	1139-30-6
	2BC4T	SVOC	12.59	2.1	43	unknown	n/a	n/a
	2BC4T	SVOC	16.75	0.95	50	unknown	n/a	n/a
	5BC4T	SVOC	8.71	1	96	benzaldehyde,4-hydroxy-	C7H6O2	123-08-0
	5BC4T	SVOC	9.26	0.82	98	phenol,3,4-dimethoxy-	C8H10O3	2033-89-8
	5BC4T	SVOC	9.56	0.85	83	benzeacetic acid, .alpha., 4-dihydroxy-	C8H8O4	1198-84-1
	5BC4T	SVOC	10.91	1.1	83	phenol,4- (3-hydroxy-1-propenyl)-	C9H10O2	5/9/3690
	5BC4T	SVOC	11.08	1.6	83	Benzeneacetic acid truncated	C9H10O4	306-08-1

Table Continued

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	5BC4T	SVOC	11.76	12	37	unknown	n/a	n/a
	5BC4T	SVOC	12.59	1	91	1- hexadecanol	C16H34O	36653-82-4
	5BC4T	SVOC	12.59	1	91	1-heptadecanol	C17H36O	1454-85-9
	5BC4T	SVOC	15.04	0.94	81	cyclododecyne	C12H2O	1129-90-4
	5BC4T	SVOC	16.13	0.95	25	unknown	n/a	n/a
	5BC4T	SVOC	16.54	1.6	95	podocarpa-8,11,1 truncated	C21H30O2	18326-16-4
	5BC4T	SVOC	21.29	1.2	46	unknown	n/a	n/a
	5BC4T	SVOC	21.99	2.2	94	(+) Lariciresinol	C20H24O6	27003-73-2
	3BC4T	SVOC	6.61	0.83	97	bicyclo [2.2.1] heptan truncated	C10H18O	1632-73-1
	3BC4T	SVOC	9.27	0.98	97	Phenol,3,4 -dimethoxy-	C8H10O3	2033-89-8
	3BC4T	SVOC	11.02	1.2	93	1H- cyclopropa [a] truncated	C15H24	17334-55-3
	3BC4T	SVOC	11.08	2.3	81	Benzeneacetic acid, 4-hydroxy-3-methoxy-	C9H10O4	306-08-1
	3BC4T	SVOC	12.59	2.2	46	unknown	n/a	n/a
	3BC4T	SVOC	12.87	0.9	98	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	1BC4T	SVOC	15.78	1.8	91	aflatoxin M2	C17H14O7	6885-57-0
33% COC	4CY5T	VOC	15.99	.034	93	Copaene	C15H24	3856-25-5
	5CY5T	VOC	11.85	.094	50	unknown	n/a	n/a
	1BC5T	VOC	NONE					
	5BC6T	VOC	12.17	.065	95	Benzene, 1,2-dimethyl-	C8H10	95-47-6
	5BC6T	VOC	12.17	.065	95	Benzene, 1,3-dimethyl-	C8H10	108-38-3
	5BC6T	VOC	14.35	.039	91	Benzene, 1,2,4-trimethyl-	C9H12	95-63-6
	5BC6T	VOC	14.35	.039	91	Benzene,1,2,3-trimethyl	C9H12	526-73-8
	4CY5T	SVOC	NONE					
	5CY5T	SVOC	11.78	2.000	46	unknown	n/a	n/a

Table Continued

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	5CY5T	SVOC	12.1	.840	35	unknown	n/a	n/a
	5CY5T	SVOC	12.62	.830	96	Cyclotetradecane	C14H28	295-17-0
	5CY5T	SVOC	12.91	900	99	Hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	5CY5T	SVOC	14.71	1.400	64	unknown	n/a	n/a
	5CY5T	SVOC	20.21	2.800	96	10-Nonadecanone	C19H38O	504-57-4
	5CY5T	SVOC	21.04	2.500	78	2(3h) -FORANONE, D truncated	C20H22O6	580-72-3
	5BC6T	SVOC	6.61	1.600	96	bicyclo[2.2.1] heptan-2-ol,1,3,3-trimethyl-	C10H18O	1632-73-1
	5BC6T	SVOC	6.61	1.600	96	D-fenchyl alcohol	C10H18O	1632-73-1
	5BC6T	SVOC	8.11	1.200	98	bicyclo[2.2.1] heptan truncated	C12H20O2	4057-31-2
	5BC6T	SVOC	8.11	1.200	98	endobornyl acetate	C12H20O2	76-49-3
	5BC6T	SVOC	8.11	1.200	98	.alpha.-fenchyl acetate	C12H20O2	4057-31-2
	5BC6T	SVOC	10.34	.840	91	1,6,10- dodecatrien -3-ol,3,7,11 -trimethyl -,	C15H26O	142-50-7
	5BC6T	SVOC	10.34	.840	91	Farnesol	C15H26O	4602-84-0
	5BC6T	SVOC	10.34	.840	91	d-Nerolidol	C15H26O	142-50-7
	5BC6T	SVOC	10.34	.840	91	Nerolidol isomer	C15H26O	0-00-0
	5BC6T	SVOC	11.02	.890	97	1H-Cyclopropa [a] truncated	C15H24	17334-55-3
	5BC6T	SVOC	11.02	.890	97	Calarene	C15H24	17334-55-3
	5BC6T	SVOC	11.09	.890	81	Benzeneacetic acid, 4-hydroxy -3methoxy -	C9H10O4	306-08-1
	5BC6T	SVOC	11.2	1.400	58	unknown	n/a	n/a
	5BC6T	SVOC	12.6	1.300	41	unknown	n/a	n/a
	5BC6T	SVOC	12.87	1.500	97	Hexadecanoic acid truncated	C17H34O2	112-39-0

Table Continued

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	5BC6T	SVOC	13.98	2.400	97	9,12 - Octadecadienoic truncated	C19H34O2	2566-97-4
	1BC5T	SVOC	11.08	1.700	80	Benzeneacetic acid, 4hydroxy-3-methoxy-	C9H10O4	306-08-1
	1BC5T	SVOC	11.74	2.000	38	unknown	n/a	n/a
	1BC5T	SVOC	12.58	1.900	42	unknown	n/a	n/a
	1BC5T	SVOC	12.88	1.200	99	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	1BC5T	SVOC	13.97	1.200	99	8,10 - octadecadienoic acid, methyl ester	C19H34O2	56599-58-7
	1BC5T	SVOC	14.67	1.400	80	dihydro-neoclorene - (11)	C15H26	0-00-0
	1BC5T	SVOC	15.04	1.400	89	Cyclododecyne	C12H20	1129-90-4
	1BC5T	SVOC	17.82	2.100	60	unknown	n/a	n/a

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – March 2007 Water Oak Roots

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
100% COC								
	3WO3R	VOC	NONE					
	2WO3R	VOC	NONE					
	4WO3R	VOC	NONE					
	1WO3R	VOC	3.26	.029	83	acetone	C3H6O	67-64-1
	1WO3R	VOC	3.47	.038	78	isopropyl alcohol	C3H8O	67-63-0
	3WO3R	SVOC	8.46	1.300	78	.alpha.-d-ribopyranoside, methyl-	C6H12O5	0-00-0
	3WO3R	SVOC	12.99	.960	89	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	3WO3R	SVOC	18.87	1.100	52	unknown	n/a	n/a
	3WO3R	SVOC	23.17	22.000	68	unknown	n/a	n/a
	3WO3R	SVOC	23.36	8.800	46	unknown	n/a	n/a
	2WO3R	SVOC	2.89	1.200	80	1,2 propanediol	C3H8O2	57-55-6
	2WO3R	SVOC	3.34	1.200	90	2,3-butanediol	C4H10O2	513-85-9
	2WO3R	SVOC	5.42	1.000	50	unknown	n/a	n/a
	2WO3R	SVOC	5.85	.870	90	benzeacetaldehyde	C8H8O	122-78-1
	2WO3R	SVOC	7.77	.990	35	unknown	n/a	n/a
	2WO3R	SVOC	8.65	1.500	86	.alpha.-d-ribopyranoside, methyl-	C6H12O5	0-00-0
	2WO3R	SVOC	9.1	1.900	72	unknown	n/a	n/a
	2WO3R	SVOC	9.5	26.000	56	unknown	n/a	n/a
	2WO3R	SVOC	10.6	1.1	55	unknown	n/a	n/a
	2WO3R	SVOC	10.74	1	47	unknown	n/a	n/a
	2WO3R	SVOC	11.89	2.4	35	unknown	n/a	n/a
	2WO3R	SVOC	12.21	1.2	25	unknown	n/a	n/a
	2WO3R	SVOC	12.48	1.4	70	unknown	n/a	n/a
	2WO3R	SVOC	12.95	0.9	78	1-dimethylamino-1,1-dihydro-2-truncated	C14H16N2	80569-38-6
	2WO3R	SVOC	13.02	0.83	80	decanoic acid, methyl ester	C11H22O2	110-42-9

Table Continued

Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	2WO3R	SVOC	13.28	1.6	55	unknown	n/a	n/a
	2WO3R	SVOC	14.24	1.2	72	unknown	n/a	n/a
	4WO3R	SVOC	13.01	1.3	93	hexadecanoic acid, methyl ester	C17H34O2	112-39-0
	4WO3R	SVOC	14.16	1.3	35	unknown	n/a	n/a
	4WO3R	SVOC	14.28	1.4	83	2-isopropyl-4,5,6- trimethyl -3-nitroaniline	C12H18N2O2	68904-09-6
	4WO3R	SVOC	17.87	1.7	38	unknown	n/a	n/a
	4WO3R	SVOC	18.01	1.2	49	unknown	n/a	n/a
	4WO3R	SVOC	18.22	1.4	46	unknown	n/a	n/a
	1WO3R	SVOC	18.22	0.89	42	unknown	n/a	n/a

Summary of Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 1 Water Oak Tops

Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
3WO3T	VOC	NONE					
2WO3T	VOC	3.352	28.98	94	Dimethyl sulfide	C2H6S	75-18-3
4WO3T	VOC	NONE					
1WO3T	VOC	NONE					
3WO3T	SVOC	8.54	1100	78	.alpha.-d-ribopyranoside, methyl-	C6H12O5	0-00-0
3WO3T	SVOC	9.01	1000	72	unknown	N/A	N/A
3WO3T	SVOC	10.73	1200	58	unknown	N/A	N/A
3WO3T	SVOC	11.65	1000	38	unknown	N/A	N/A
3WO3T	SVOC	19.75	3200	47	unknown	N/A	N/A
3WO3T	SVOC	23.74	5400	58	unknown	N/A	N/A
2WO3T	SVOC	5.85	830	78	benzeneacetaldehyde	C8H8O	122-78-1
2WO3T	SVOC	8.49	1300	78	.alpha.-d-ribopyranoside, methyl-	C6H12O5	0-00-0
2WO3T	SVOC	23.42	4500	83	.delta.-guaiene	C15H24	3691-11-0
2WO3T	SVOC	23.64	5600	47	unknown	N/A	N/A
4WO3T	SVOC	8.53	810	78	.alpha.-d-ribopyranoside, methyl-	C6H12O5	0-00-0
4WO3T	SVOC	12.92	860	81	Homosalate	C16H22O3	118-56-9
4WO3T	SVOC	19.59	1300	53	unknown	N/A	N/A
1WO3T	SVOC	9.66	910	30	unknown	N/A	N/A
1WO3T	SVOC	10.74	1800	47	unknown	N/A	N/A
1WO3T	SVOC	11.4	1000	30	unknown	N/A	N/A
1WO3T	SVOC	11.67	1300	53	unknown	N/A	N/A
1WO3T	SVOC	12.95	830	60	unknown	N/A	N/A
1WO3T	SVOC	13.52	910	30	unknown	N/A	N/A
1WO3T	SVOC	14.24	910	72	unknown	N/A	N/A

Year 1 – Initial Media Tics

Sample ID	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
BL04	7.35	0.11	86	octanoic acid	C8H16O2	124-07-2
BL04	8.14	0.32	89	nonanoic acid	C9H18O2	112-05-0
BL02	12.47	0.53	99	hexadecanoic acid	C16H32O2	57-10-3
BL01	15.31	1.1	98	1-docosene	C22H44	1599-67-3
BL02	15.31	0.55	98	cyclohexadecane	C16H32	295-65-8
BL03	15.29	0.72	96	cyclohexadecane	C16H32	295-65-8
BL04	15.30	0.11	96	cyclopentadecane	C15H30	295-48-7
BL01	16.30	0.74	64	Unknown		
BL02	16.30	0.42	93	cyclotetracosane	C24H48	297-03-0
BL03	16.29	0.49	91	1-nonadecanol	C19H40O	1454-84-8
BL01	17.21	1.9	95	hexadecane	C16H34	544-76-3
BL02	17.20	0.63	93	eicosane, 10-methyl	C21H44	54833-23-7
BL03	17.19	0.93	96	octadecane	C18H38	13475-75-7
BL04	17.19	0.12	98	heneicosane	C21H44	629-94-7
BL01	17.26	1.1	95	1-eicosonol	C20H42O	629-96-9
BL02	17.26	0.43	96	cyclotetracosane	C24H48	297-03-0
BL03	17.24	0.58	98	cyclotetracosane	C24H48	297-03-0
BL01	18.15	1.9	94	heptadecane	C17H36	629-78-7
BL02	18.15	0.76	95	heptadecane	C17H36	629-78-7
BL03	18.14	0.96	95	octodecane	C18H38	593-45-3
BL04	18.13	0.15	96	eicosane	C20H42	112-95-8
BL01	18.50	1.8	91	chlorophene	C13H11ClO	120-32-1
BL02	18.50	0.98	92	chlorophene	C13H11ClO	120-32-1
BL03	18.48	1.0	43	Unknown		
BL04	18.47	0.19	83	chlorophene	C13H11ClO	120-32-1
BL01	18.69	0.84	55	Unknown		
BL02	18.68	0.49	78	5.beta.Pregn-11-ene	C21H34	6673-73-0
BL03	18.67	0.59	50	Unknown		
BL04	18.66	0.097	78	5.beta.Pregn-11-ene	C21H34	6673-73-0

There are peaks from the raw data that are not shown in this table. These peaks are unknown (Quality factor < 75).

Year 1 – Final Media Tics

Summary of Tentatively Identified Compounds (TICs) in Final Media Samples – Year 1

Species and Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
BW - 100% COC	1BW3	SVOC	19.09	0.0143	35	Unknown	n/a	n/a
	2BW3		None					
	2BW-3 (BD-2)		None					
	3BW3	SVOC	19.07	0.0111	25	Unknown	n/a	n/a
	3BW3	SVOC	20.77	0.0153	27	Unknown	n/a	n/a
	3BW3	SVOC	21.06	0.0112	47	Unknown	n/a	n/a
	4BW3		None					
BW - 67% COC	2BW4	SVOC	19.09	0.018	41	Unknown	n/a	n/a
	2BW4	SVOC	20.00	0.00014	0	Unknown	n/a	n/a
	2BW4	SVOC	20.80	0.016	32	Unknown	n/a	n/a
	3BW4	SVOC	21.61	0.0187	47	Unknown	n/a	n/a
	3BW4	SVOC	21.70	0.0318	41	Unknown	n/a	n/a
	4BW4	SVOC	21.80	0.022	46	Unknown	n/a	n/a
	4BW4	SVOC	21.70	0.051	38	Unknown	n/a	n/a
	5BW4	SVOC	19.09	0.014	41	Unknown	n/a	n/a
	5BW4	SVOC	21.70	0.027	46	Unknown	n/a	n/a
BW - 33% COC	1BW6	SVOC	21.08	0.014	60	Unknown	n/a	n/a
	2BW6	SVOC	20.80	0.012	15	Unknown	n/a	n/a
	4BW6	SVOC	19.09	0.011	0	Unknown	n/a	n/a
	5BW5	SVOC	19.08	0.01	22	Unknown	n/a	n/a
BC - 100% COC	2BC3	SVOC	15.29	0.0123	38	Unknown	n/a	n/a
	2BC3	SVOC	20.92	0.0105	38	Unknown	n/a	n/a
	3BC3		None				Table Continued	

Species and Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	4BC3		None					
	5BC3		None					
	5BC3 (BD-1)	VOC	10.66	0.0203	96	.alpha.-Pinene, (-) -	C10H16	80-56-8
BC - 67% COC	1BC4	SVOC	18.19	0.0156	99	1-Docosene	C22H44	1599-67-3
	1BC4	SVOC	18.28	0.0112	53	Unknown	n/a	n/a
	1BC4	SVOC	19.78	0.0281	38	Unknown	n/a	n/a
	1BC4	SVOC	21.82	0.0151	43	Unknown	n/a	n/a
	1BC4	SVOC	22.04	0.0259	43	Unknown	n/a	n/a
	2BC4	SVOC	12.59	0.0106	98	1-Heptadecene	C17H34	6765-39-5
	2BC4	SVOC	12.93	0.0173	55	Unknown	n/a	n/a
	2BC4	SVOC	14.00	0.0117	53	Unknown	n/a	n/a
	2BC4	SVOC	19.00	0.0117	91	1-Eicosanol	C20H42O	629-96-9
	3BC4	VOC	None					
	5BC4	SVOC	12.60	0.0139	98	1-Octadecene	C18H36	112-88-9
	5BC4	SVOC	18.12	0.0205	10	Unknown	n/a	n/a
BC - 33% COC	1BC5	SVOC	20.88	0.0125	38	Unknown	n/a	n/a
	4CY5	SVOC	12.13	0.0106	46	Unknown	n/a	n/a
	4CY5	SVOC	16.17	0.0143	96	5-Eicosene, (E) -	C20H40	74685-30-6
	4CY5	SVOC	17.18	0.0152	98	Cyclotetracosane	C24H48	297-03-0
	4CY5	SVOC	18.20	0.0281	99	1-Docosane	C22H44	1599-67-3
	4CY5	SVOC	18.29	0.0130	53	Unknown	n/a	n/a
	4CY5	SVOC	19.02	0.0103	93	16-Octadecanal	C18H34O	56554-87-1
	4CY5	SVOC	19.79	0.0499	30	Unknown	n/a	n/a
	4CY5	SVOC	21.09	0.0406	56	Unknown	n/a	n/a
	4CY5	SVOC	21.84	0.0228	22	Unknown	n/a	n/a

Table Continued

Species and Water Trt.	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
	4CY5	SVOC	22.06	0.0764	43	Unknown	n/a	n/a
	5CY5	VOC	None					
	5BC6	SVOC	15.28	0.0133	38	Unknown	n/a	n/a
	5BC6	SVOC	20.61	0.0102	4	Unknown	n/a	n/a
ERC - 100% COC	1ERC3		None					
	3ERC3	SVOC	11.01	0.0160	49	Unknown	n/a	n/a
	3ERC3	SVOC	11.87	0.0186	55	Unknown	n/a	n/a
	3ERC3	SVOC	15.45	0.0193	18	Unknown	n/a	n/a
	3ERC3	SVOC	17.50	0.0150	2	Unknown	n/a	n/a
	3ERC3	SVOC	17.53	0.0211	64	Unknown	n/a	n/a
	3ERC3	SVOC	17.79	0.0130	94	Tetracosane	C24H50	646-31-1
	3ERC3	SVOC	18.89	0.0190	93	Heptadecane	C17H36	629-78-7
	3ERC3	SVOC	19.38	0.0154	52	Unknown	n/a	n/a
	4ERC3	VOC	10.10	0.0490	97	Sabinene	C10H16	3387-41-5
	4ERC3	SVOC	17.53	0.0160	43	Unknown	n/a	n/a
	4ERC3	SVOC	20.86	0.0102	25	Unknown	n/a	n/a
	5ERC3	SVOC	17.52	0.0211	0	Unknown	n/a	n/a
	5ERC3	SVOC	17.54	0.0143	78	Tetradecanal	C14H28O	124-25-4
	5ERC3	SVOC	18.61	0.0108	45	Unknown	n/a	n/a
	5ERC3	SVOC	18.90	0.0151	91	Heneicosane	C21H44	629-94-7
WO - 100% COC	1WO3		None					
	2WO3		None					
	3WO3	VOC	11.33	0.0115	97	.beta.-Phellandrene	C10H16	555-10-2
	4WO3		None					

Notes: there are peaks from the raw data that are not shown in this table. Peaks present in the corresponding control samples are not shown. Also peaks with estimated concentration less than 0.010mg/kg are not shown in this table. Peaks labeled as “Unknown” in this table have a Quality factor that is less than 75, and the identity provided in the raw data is very unreliable.

Year 2 – Initial Plant Tics

Summary of SVOC Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 2

Sample ID	Sample type	SVOC or VOC	Peak RT (min)	Estimated conc. (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
I BC1	root	SVOC				none		
I BC2	root	SVOC	15.21	21.00	90	4,4-dimethyl-13.alpha.-androst-5-ene	C21H34	73495-94-0
			21.80	22.00	93	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
I BC3	root	SVOC	9.27	30.00	95	Cyclodane	C10H20	872-05-9
I BC4	root	SVOC	9.26	43.00	94	1-decene	C10H20	872-05-9
I BW1	root	SVOC	7.01	30.00	91	1,2-Benzenediol	C6H6O2	120-80-9
			7.68	49.00	94	Salicyl alcohol	C7H8O2	90-01-7
			21.81	30.00	95	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
I BW2	root	SVOC	5.52	43.00	83	5,6-dihydro-2H-pyran-2-one	C5H6O2	3393-45-1
			5.68	3.70	95	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8
			7.03	9.80	91	1,2-Benzenediol	C6H6O2	120-80-9
			7.81	66.00	95	Salicyl alcohol	C7H8O2	90-01-7
			11.12	3.80	91	Hexadecanol	C16H34O2	29354-98-1
			12.87	6.10	99	Hexadecanoic acid	C16H32O2	57-10-3
			21.84	23.00	97	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
I BW3	root	SVOC	5.16	8.80	83	6-chloro-2-heptane	C7H13Cl	92639-28-6
			5.67	3.30	97	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8
			7.02	13.00	91	1,2-Benzenediol	C6H6O2	120-80-9
			7.69	39.00	94	Salicyl alcohol	C7H8O2	90-01-7
			11.11	5.10	91	Tetradecanal	C14H28O	124-25-4
			12.85	5.20	98	Hexadecanoic acid	C16H32O2	57-10-3
			21.82	27.00	86	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
I BW4	root	SVOC	5.69	2.10	97	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8
			5.85	1.10	95	1,2-cyclohexanediol,trans-	C6H12O2	1460-57-7

Table Continued

Sample ID	Sample type	SVOC or VOC	Peak RT (min)	Estimated conc. (mg/kg)	Quality Factor	Chemical Name	Chemical Formula	CAS No.
			7.04	7.70	94	1,2-Benzenediol	C6H6O2	120-80-9
			7.80	39.00	95	Salicyl alcohol	C7H8O2	90-01-7
			11.13	3.10	90	Hexadecanol	C16H34O2	29354-98-1
			12.86	1.90	97	Hexadecanoic acid	C16H32O2	57-10-3
			21.83	13.00	95	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
			23.20	4.40	95	Epifriedelinol	C30H52O	16844-71-6
I CW1	root	SVOC	5.23	2.00	91	Cyclohexanone, 2-hydroxy-	C6H10O2	533-60-8
			5.71	56.00	94	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8
			5.91	4.60	95	1,2-cyclohexanediol,trans-	C6H12O2	1460-57-7
			6.88	3.40	95	Benzoic acid	C7H6O2	65-85-0
			7.04	17.00	94	1,2-Benzenediol	C6H6O2	120-80-9
			7.70	21.00	94	Salicyl alcohol	C7H8O2	90-01-7
			11.12	4.20	91	Hexadecanol	C16H34O2	29354-98-1
			12.83	2.20	99	Hexadecanoic acid	C16H32O2	57-10-3
			21.26	2.10	97	Ergost-5-en-3-ol, (3.beta.)-	C28H48O	4651-51-8
			21.83	19.00	97	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
I CW2	root	SVOC	5.67	38.00	95	Benzaldehyde, 2-hydroxy-	C7H6O2	90-02-8
			7.00	30.00	91	1,2-Benzenediol	C6H6O2	120-80-9
			7.65	26.00	91	Salicyl alcohol	C7H8O2	90-01-7
			21.80	20.00	95	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
I CW3	root	SVOC	6.99	18.00	91	1,2-Benzenediol	C6H6O2	120-80-9
			7.63	18.00	95	Salicyl alcohol	C7H8O2	90-01-7
			9.26	17.00	94	1-decene	C10H20	872-05-9
			21.80	26.00	96	stigmast-5-en-3-ol, (3.beta.,24S)	C29H50O	83-47-6
I CW4	root	SVOC				none		

Summary of VOC Tentatively Identified Compounds (TICs) in Initial Plant Tissue Samples – Year 2

Sample ID	Sample type	SVOC or VOC	Peak RT (min)	Estimated. concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	CAS No.
IBC1	root	VOC	2.893	0.138	74	ethanol	C2H6O	64-17-5
			3.658	0.084	86	Acetic acid, methyl ester	C3H6O2	79-20-9
I BC2	root	VOC	1.969	0.042	74	Acetaldehyde	C2H4O	75-07-0
			2.808	0.308	90	ethanol	C2H6O	64-17-5
I BC3	root	VOC	1.969	0.050	83	Acetaldehyde	C2H4O	75-07-0
			2.808	0.327	74	ethanol	C2H6O	64-17-5
I BC4	root	VOC	1.962	0.080	74	Acetaldehyde	C2H4O	75-07-0
			2.801	0.353	90	ethanol	C2H6O	64-17-5
I BW1	root	VOC	1.952	0.056	90	Acetaldehyde	C2H4O	75-07-0
			3.304	0.359	91	Dimethyl sulfide	C2H6S	75-18-3
I BW2	root	VOC	2.001	0.228	90	Acetaldehyde	C2H4O	75-07-0
			3.342	0.415	91	Dimethyl sulfide	C2H6S	75-18-3
I BW3	root	VOC	1.96	0.032	74	Acetaldehyde	C2H4O	75-07-0
			2.799	0.479	90	ethanol	C2H6O	64-17-5
			3.302	0.273	94	Dimethyl sulfide	C2H6S	75-18-3
I BW4	root	VOC	1.981	0.144	90	Acetaldehyde	C2H4O	75-07-0
			3.322	0.303	91	Dimethyl sulfide	C2H6S	75-18-3
I CW1	root	VOC	1.97	0.159	90	Acetaldehyde	C2H4O	75-07-0
			2.809	1.201	90	ethanol	C2H6O	64-17-5
			3.312	0.045	91	Dimethyl sulfide	C2H6S	75-18-3
			15.396	0.107	97	Benzaldehyde, 2- hydroxy-	C7H6O2	90-02-8
I CW2	root	VOC	1.973	0.063	90	Acetaldehyde	C2H4O	75-07-0
			2.811	0.484	90	ethanol	C2H6O	64-17-5
			3.325	0.028	86	ethanethiol	C2H6S	75-08-1
I CW3	root	VOC	1.963	0.048	74	Acetaldehyde	C2H4O	75-07-0
			2.801	0.117	83	ethanol	C2H6O	64-17-5
			15.399	0.219	96	Benzaldehyde, 2- hydroxy-	C7H6O2	90-02-8
I CW4	root	VOC				none		

Year 2- Final Plant Tics

Summary of SVOC Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 2

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
DI	II DI 2 BC R	SVOC	6.12	2NJ	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-2-8
			6.31	1.4NJ	94	1, 2 - cyclohexane diol, trans -	C6H12O2	1460-57-7
			7.55	0.99NJ	91	1,2 - benzenediol	C6H6O2	120-80-9
			8.22	2.3NJ	95	salicyl alcohol	C7H8O2	90-01-7
			9.75	0.86NJ	95	1-decene	C10H20	872-05-9
			11.6	1.1NJ	91	hexadecanol	C16H34O	29354-98-1
			22.64	2.7NJ	86	.gamma. - sitosterol	C29H50O	83-47-6
DI	III DI 2 BC R	SVOC	7.25	1.3NJ	91	borneol	C10H18O	507-70-0
			22.62	6NJ	90	.gamma. - sitosterol	C29H50O	83-47-6
DI	III DI 1 BC R	SVOC	8.18	5.2NJ	95	salicyl alcohol	C7H8O2	90-01-7
			15.74	1NJ	90	3,6 - di-tert-butyl -1,7 - dihydroxy - 8-methylnapthalene	C19H26O2	83021-63-0
			22.6	10NJ	74	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
DI	I DI 3 BC R	SVOC	6.11	1.1NJ	95	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			6.29	1.8NJ	95	1,2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			7.52	1NJ	94	1,2 - benzendiol	C6H6O2	120-80-9
			8.19	6.8NJ	96	salicyl alcohol	C7H8O2	90-01-7
			22.59	1.9NJ	98	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
DI	I DI 2 BW R	SVOC	2.98	1.5NJ	90	2-butanone, 3 -hydroxy -	C4H8O2	513-86-0
			5.47	1.2NJ	87	3- octanone	C8H16O	106-68-3

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			6.33	4.6NJ	94	cis -1,2 - cyclohexanediol	C6H12O2	1792-81-0
			7.53	2.1NJ	91	1,2 - benzenediol	C6H6O2	120-80-9
			8.23	11NJ	95	salicyl alcohol	C7H8O2	90-01-7
			8.45	0.82NJ	96	salicylic acid	C7H6O3	69-72-7
			11.39	0.9NJ	91	cyclododecane	C12H24	294-62-2
			11.57	2NJ	91	hexadecanol	C16H34O	29354-98-1
			18.71	2.5NJ	97	eicosane	C20H42	112-95-8
			22.61	14NJ	92	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
DI	I DI 1 BW R	SVOC	7.58	4.8NJ	94	1,2 - benzenediol	C6H6O2	120-80-9
			8.31	18NJ	95	salicyl alcohol	C7H8O2	90-01-7
			11.4	0.9NJ	96	cyclododecane	C12H24	294-62-2
			11.58	1.2NJ	91	pentadecanal -	C15H30O	2765-11-9
DI	I DI 3 BW R	SVOC	6.09	0.8NJ	93	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			6.37	5NJ	87	1,2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			7.57	1.2NJ	91	1,2 - benzendiol	C6H6O2	120-80-9
			8.29	12NJ	95	salicyl alcohol	C7H8O2	90-01-7
			9.74	0.94NJ	95	1-decene	C10H20	872-05-9
			11.4	1NJ	91	cyclododecane	C12H24	294-62-2
			18.71	2.6NJ	96	eicosane	C20H42	112-95-8
			22.62	14NJ	78	.gamma. - sitosterol	C29H50O	83-47-6
DI	II DI 2 BW R	SVOC	2.83	1.7NJ	83	3-penten -2-ol	C5H10O	1569-50-2
			6.09	0.87NJ	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			6.3	3.3NJ	95	1, 2 - cyclohexane diol, trans -	C6H12O2	1460-57-7
			7.31	2NJ	95	benzoic acid	C7H6O2	65-85-0
			7.5	1.7NJ	94	1,2 - benzendiol	C6H6O2	120-80-9
			8.21	10NJ	95	salicyl alcohol	C7H8O2	90-01-7

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			8.43	1NJ	97	salicylic acid	C7H6O3	69-72-7
			9.74	0.99NJ	94	1-decene	C10H20	872-05-9
			13.31	2.2NJ	98	hexadecanoic acid	C16H32O2	57-10-3
			15.76	0.93NJ	96	octadecanoic acid, butyl ester	C22H44O2	123-95-5
			18.33	0.8NJ	90	octadecanal	C18H36O	638-66-4
			18.73	1.1NJ	97	eicosane	C20H42	112-95-8
DI	III DI 1 CW R	SVOC	5.73	4.7NJ	86	cyclopentane, 1,2,4 - trimethyl - (1 alpha., 2.beta., 4.alpha.)-	C8H16	16883-48-0
			6.15	14NJ	96	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			7.57	4.8NJ	89	1,2 - benzendiol	C6H6O2	120-80-9
			7.64	1.1NJ	97	benzoic acid	C7H6O2	65-85-0
			8.28	15NJ	95	salicyl alcohol	C7H8O2	90-01-7
			8.62	19NJ	96	benzoic acid , 2 -hydroxy -	C7H6O3	69-72-7
			22.59	2.6NJ	96	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
DI	II DI 2 CW R	SVOC	2.84	1.5NJ	80	3-penten -2- ol	C5H10O	1569-50-2
			4.7	1.5NJ	80	cyclopentanone	C6H10O	1120-72-5
			6.26	74NJ	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			8.19	1.1NJ	95	salicyl alcohol	C7H8O2	90-01-7
			8.31	11NJ	95	salicyl alcohol	C7H8O2	90-01-7
			8.64	20NJ	93	salicylic acid	C7H6O3	69-72-7
			9.78	0.92NJ	91	cyclododecane	C12H24	294-62-2
			13.37	1.1NJ	99	hexadecanoic acid	C16H32O2	57-10-3
			22.63	8.4NJ	89	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
DI	I DI 3 CW R	SVOC	6.19	50NJ	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			8.27	13NJ	96	salicyl alcohol	C7H8O2	90-01-7
			8.62	19NJ	94	salicylic acid	C7H6O3	69-72-7

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			22.62	6.5NJ	96	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
DI	III DI 3 CW R	SVOC	6.24	19NJ	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			8.3	9.5NJ	97	salicyl alcohol	C7H8O2	90-01-7
			8.73	35NJ	93	salicylic acid	C7H6O3	69-72-7
			9.8	0.9NJ	93	1-decene	C10H20	872-05-9
			13.36	1.3NJ	97	hexadecanoic acid	C16H32O2	57-10-3
			22.26	1.2NJ	93	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	III 50 3 BC R	SVOC	6.07	1.2NJ	96	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			6.23	1.4NJ	95	1, 2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			8.12	6.6NJ	95	salicyl alcohol	C7H8O2	90-01-7
			13.28	6.2NJ	99	hexadecanoic acid	C16H32O2	57-10-3
			14.37	2.2NJ	96	9,12 - octadecadienoic acid (2,2) -	C18H32O2	60-33-3
			15.69	1.9	91	3- diphenylphosphinoyl -3- methylbuton -2- one	C17H19O2P	50356-83-7
			21.91	1.4	89	ergost -5- en -3. beta. -ol	C28H48O	0-00-0
			22.11	1.4	93	stigmast - 5 -en -3.beta. - ol	C29H48O	38485-29-9
			22.56	17	96	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	III 50 1 BC R	SVOC	7.22	1J	87	bicyclo {2.2.1} hepton -2-ol, 1,7,7 - trimethyl - (15- endo) -	C10H18O	464-45-9
			9.26	0.88NJ	97	vanillin	C8H8O3	121-33-5
			9.71	0.91NJ	96	cyclododecane	C12H24	294-62-2
			13.32	6.2NJ	99	hexadecanoic acid	C16H32O2	57-10-3
			14.41	2.4NJ	99	9,12 -octadecadienoic acid (2,2) -	C18H32O2	60-33-3
			14.52	1.8NJ	91	octadecanoic acid	C18H36O2	57-11-4

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			17.36	2.5NJ	96	9(1H) - phenenthrenone, 2,3,4,4a,10,10a-hexahydro- 6-hydroxy -1,1,4a - trimethyl-7-	C20H28O2	511-05-7
			21.93	2.7NJ	99	ergost -5- en -3. beta. -ol	C28H48O	0-00-0
			22.13	5.2NJ	94	trans- stigmasta - 5,22 -dien -3. beta. -ol	C29H48O	0-00-0
			22.53	12NJ	89	.gamma. - sitosterol	C29H50O	83-47-6
Low	II 50 3 BC R	SVOC	6.22	0.84NJ	94	1, 2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			8.07	1.2NJ	90	salicyl alcohol	C7H8O2	90-01-7
			13.28	3.1NJ	99	hexadecanoic acid	C16H32O2	57-10-3
			20.72	1NJ	90	4,4-dimethyl-13.alpha.- androst - 5-ene	C21H34	73495-94-0
			22.58	8.4NJ	96	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	I 50 2 BC R	SVOC	8.11	4.4NJ	94	salicyl alcohol	C7H8O2	90-01-7
			11.57	1.3NJ	91	hexadecanol	C16H34O	29354-98-1
			14.39	1.3NJ	98	9,12 - octadecadienoic acid (2,2) -	C18H32O2	60-33-3
			18.3	0.86NJ	87	squalene	C30H5O	7683-64-9
			21.93	1.4NJ	97	ergost -5- en -3. beta. -ol, (3.beta.) -	C28H48O	4651-51-8
			22.61	29NJ	96	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	III 50 1 BW R	SVOC	6.27	3.2NJ	95	1, 2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			8.16	11NJ	91	salicyl alcohol	C7H8O2	90-01-7
			22.6	15NJ	95	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
Low	I 50 1 BW R	SVOC	6.28	3.6NJ	95	1, 2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			8.17	16NJ	91	salicyl alcohol	C7H8O2	90-01-7
			18.75	6.9NJ	91	octadecane	C18H38	593-45-3
			22.63	29NJ	87	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	III 50 3 BW R	SVOC	6.28	4.5NJ	95	1, 2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			8.18	16NJ	94	salicyl alcohol	C7H8O2	90-01-7
Low	II 50 1 BW R	SVOC	6.28	6.7NJ	95	1, 2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			8.18	21NJ	95	salicyl alcohol	C7H8O2	90-01-7
			18.75	21NJ	97	eicosane	C20H42	112-95-8
			22.6	18NJ	95	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	II 50 3 CW R	SVOC	2.85	2.2NJ	83	3-penten - 2- ol	C5H10O	1569-50-2
			6.17	3.2NJ	96	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			8.27	8NJ	97	salicyl alcohol	C7H8O2	90-01-7
			8.67	34NJ	93	salicylic acid	C7H6O3	69-72-7
			11.59	1.2NJ	93	octadecanal	C18H36O	638-66-4
			13.38	6.5NJ	98	hexadecanoic acid	C16H32O2	57-10-3
			14.47	1.6NJ	97	9,12 - octadecadienoic acid (2,2) -	C18H32O2	60-33-3
			16.34	1.5NJ	90	1-eicosanol	C20H42O	629-96-9
			22.64	17NJ	95	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	I 50 1 CW R	SVOC	6.18	9.5NJ	98	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			8.21	7.6NJ	95	salicyl alcohol	C7H8O2	90-01-7
			8.63	59NJ	93	salicylic acid	C7H6O3	69-72-7
			9.57	1.5NJ	96	2-propenoic acid, 3 - phenyl -	C9H8O2	621-82-9
			11.59	2.3NJ	91	pentadecanal -	C15H30O	2765-11-9
			13.33	1.5NJ	95	hexadecanoic acid	C16H32O2	57-10-3
			14.49	31NJ	97	9,12 - octadecadienoic acid (2,2) -	C18H32O2	60-33-3
			18.31	2.2NJ	89	nerolidol	C15H26O	7212-44-4
			21.97	8.1NJ	95	ergost -5- en -3. beta. -ol, (3.beta.) -	C28H48O	4651-51-8
			22.69	54NJ	99	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
Low	III 50 3 CW R	SVOC	6.2	13NJ	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			8.66	3.9NJ	93	salicylic acid	C7H6O3	69-72-7
			9.56	1.1NJ	94	2-propenoic acid, 3 - phenyl -	C9H8O2	621-82-9
			11.59	1.4NJ	91	pentadecanal -	C15H30O	2765-11-9
			13.32	3.5NJ	99	hexadecanoic acid	C16H32O2	57-10-3
			14.43	1.6NJ	95	9,12 - octadecadienoic acid (2,2) -	C18H32O2	60-33-3
			18.04	2.6NJ	94	1,4 - methanoazulene , decahydro -4,8,8 - trimethyl - 9 - methylene -, {15-(1.alpha.,3a.	C15H24	475-20-7
			22.64	16NJ	90	.gamma. - sitosterol	C29H50O	83-47-6
Low	II 50 1 CW R	SVOC	6.22	36NJ	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			7.74	1.8NJ	97	benzoic acid	C7H6O2	1863-63-4
			8.3	16NJ	94	salicyl alcohol	C7H8O2	90-01-7
			8.65	40NJ	93	salicylic acid	C7H6O3	69-72-7
			13.35	1.5NJ	99	hexadecanoic acid	C16H32O2	57-10-3

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			18.03	3.4NJ	94	.beta. - selinene	C15H24	17066-67-0
			18.33	4.5NJ	91	octadecanal	C18H36O	638-66-4
			22.58	20NJ	91	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
High	III 100 1 BC R	SVOC	7.25	2NJ	90	borneol	C10H18O	507-70-0
			9.31	0.84NJ	98	benzaldehyde, 4 - hydroxy -3-methoxy -	C8H8O3	121-33-5
High	II 100 2 BC R	SVOC	7.24	1.2NJ	91	endo-borneol	C10H18O	507-70-0
			16.51	3.3NJ	87	9(1H) - phenenthrenone,2,3,4,4a,10,10a-hexahydro- 6-hydroxy -1,1,4a - trimethyl-7-	C20H28O2	511-05-7
			17.48	2.6NJ	96	9(1H) - phenenthrenone,2,3,4,4a,10,10a-hexahydro- 6-hydroxy -1,1,4a - trimethyl-7-	C20H28O2	511-05-7
			19.56	1.3NJ	94	benzo {a} pyrene	C20D12	0-00-0
			21.61	2NJ	89	sesamin	C20H18O6	0-00-0
			22.63	1.8NJ	93	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
High	I 100 1 BC R	SVOC	3.02	1.2NJ	90	2-butanone, 3 - hydroxy -	C4H8O2	513-86-0
			16.5	2.1NJ	78	2(1-h) - phenanthrenone, 3,4,4a,9,10,10a-hexahydro -6-hydroxy -1,1, 4a-trimethyl - 7-	C20H28O2	472-37-7
High	I 100 2 BC R	SVOC	8.19	1.6NJ	94	salicyl alcohol	C7H8O2	90-01-7
			11.59	1.3NJ	91	hexadecanol	C16H34O	29354-98-1

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			22.62	2.9NJ	80	.gamma. - sitosterol	C29H50O	83-47-6
High	III 100 2 BW R	SVOC	5.88	11NJ	80	2-cyclohexen-1-one	C6H8O	930-68-7
			6.3	8.5NJ	90	1, 2 - cyclohexanediol	C6H12O2	931-17-9
			8.2	14NJ	96	salicyl alcohol	C7H8O2	90-01-7
High	BD ROOT	SVOC	6.28	3.8NJ	90	cis-1,2 -cyclohexanediol	C6H12O2	1792-81-0
			8.18	7.3NJ	94	salicyl alcohol	C7H8O2	90-01-7
High	I 100 3 BW R	SVOC	8.26	6.1NJ	96	salicyl alcohol	C7H8O2	90-01-7
			18.31	1.3NJ	86	5,9,13 -pentadecatrien -2-one, 6,10, 14- trimethyl -, (e,e) -	C18H30O	1117-52-8
			22.63	3.5NJ	91	stigmast-5-en-3-ol, (3.beta.,24S)-	C29H50O	83-47-6
High	III 100 1 BW R	SVOC	6.27	5.8NJ	91	1, 2 - cyclohexanediol, trans -	C6H12O2	1460-57-7
			8.17	11NJ	96	salicyl alcohol	C7H8O2	90-01-7
High	I 100 2 BW R	SVOC	8.16	12	96	salicyl alcohol	C7H8O2	90-01-7
High	I 100 2 CW R	SVOC	6.17	8.5	95	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			6.32	5.5	96	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			7.66	28	76	1,2 - benzenediol	C6H6O2	120-80-9
			8.28	4	94	salicyl alcohol	C7H8O2	90-01-7
			9.65	1.3	93	2-propenoic acid, 3 - phenyl -	C9H8O2	621-82-9
			11.41	0.9	93	cyclododecane	C12H24	294-62-2
			11.59	1.4	91	pentadecanal -	C15H30O	2765-11-9

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			22.62	7.5	95	.gamma. - sitosterol	C29H50O	83-47-6
High	I 100 3 CW R	SVOC	6.21	110	98	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			7.8	2	96	benzoic acid	C7H6O2	1863-63-4
			8.69	30	89	salicylic acid	C7H6O3	69-72-7
			11.61	6.6	91	tetradecanal	C14H28O	124-25-4
			12.9	4.2	90	9,12,15 - octadecatrienoic acid, methyl ester, (Z,Z,Z) -	C19H32O2	301-00-8
High	III 100 2 CW R	SVOC	3.01	1.3	90	2-butanone, 3-hydroxy -	C4H8O2	513-86-0
			6.32	51	95	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			6.42	8.8	96	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			8.25	1.1	96	salicyl alcohol	C7H8O2	90-01-7
			8.34	1.5	95	salicyl alcohol	C7H8O2	90-01-7
			8.82	19	94	salicylic acid	C7H6O3	69-72-7
			11.4	2.1	96	9h- xanthene	C13H10O	92-83-1
			14.54	3.1	83	9,12 - octadecadienoic acid (Z,Z) -	C18H32O2	60-33-3
			18.33	2.6	87	5,9,13 - pentadecatrien -2-one,6,10,14 - trimethyl-	C18H30O	1117-52-8
			22.64	6.7	78	.gamma. - sitosterol	C29H50O	83-47-6
High	II 100 2 CW R	SVOC	6.22	96	97	benzaldehyde, 2-hydroxy -	C7H6O2	90-02-8
			8.23	4.3	95	salicyl alcohol	C7H8O2	90-01-7
			8.67	30	89	salicylic acid	C7H6O3	69-72-7
			11.6	2	91	hexadecanol	C16H34O	29354-98-1
			16.35	2.4	91	1-docosene	C22H44	1599-67-3
			18.06	6.9	91	1,4 - methanoazulene, decahydro - 4,8,8- trim	C15H24	475-20-7

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			18.78	1.6	91	caryophyllene	C15H24	87-44-5
			21.25	3	89	sylvenone	C14H24O	0-00-0
			21.32	6.4	83	sylvenone	C14H24O	0-00-0

Summary of VOC Tentatively Identified Compounds (TICs) in Final Plant Tissue Samples – Year 2

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
DI	II DI 2 BC R	VOC	2.01	0.04914	74	acetaldehyde	C2H4O	75-07-0
			2.85	0.03368	74	ethanol	C2H6O	64-17-5
			3.33	0.11454	94	dimethyl sulfide	C2H6S	75-18-3
			15.4	0.04705	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
DI	III DI 2 BC R	VOC	1.98	0.07839	74	acetaldehyde	C2H4O	75-07-0
			10.74	0.08887	90	hexanol	C6H12O	66-25-1
			14.62	0.04309	95	d-limonene	C10H16	5989-27-5
DI	III DI 1 BC R	VOC	2.01	0.0357	74	acetaldehyde	C2H4O	75-07-0
			2.85	0.03162	74	ethanol	C2H6O	64-17-5
			3.33	0.06231	94	dimethyl sulfide	C2H6S	75-18-3
DI	I DI 3 BC R	VOC	1.98	0.04361	74	acetaldehyde	C2H4O	75-07-0
			3.3	0.07518	94	dimethyl sulfide	C2H6S	75-18-3
DI	I DI 3 BW R	VOC	1.97	0.12036	90	acetaldehyde	C2H4O	75-07-0
			3.3	0.20127	94	dimethyl sulfide	C2H6S	75-18-3
			14.35	0.09286	87	3-octanone	C8H16O	106-68-3
DI	II DI 2 BW R	VOC	2	0.09137	90	acetaldehyde	C2H4O	75-07-0
			2.84	0.10255	90	ethanol	C2H6O	64-17-5
			3.32	0.23043	91	dimethyl sulfide	C2H6S	75-18-3
			14.36	0.15788	91	3-octanone	C8H16O	106-68-3
DI	I DI 2 BW R	VOC	1.98	0.22435	90	acetaldehyde	C2H4O	75-07-0

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			2.81	0.04819	94	ethanol	C2H6O	64-17-5
			3.3	0.10837	94	dimethyl sulfide	C2H6S	75-18-3
			9.59	0.19114	97	1-octene	C8H16O	111-66-0
			14.36	1.60081	94	3-octanone	C8H16O	106-68-3
			14.47	0.12252	90	3-octanol	C8H18O	589-98-0
			14.58	0.03414	80	octanal	C8H16O	124-13-0
			15.41	0.1067	83	1-octanol	C8H18O	111-87-5
DI	I DI 1 BW R	VOC	1.97	0.15977	90	acetaldehyde	C2H4O	75-07-0
			2.81	0.37346	90	ethanol	C2H6O	64-17-5
			3.3	0.29856	94	dimethyl sulfide	C2H6S	75-18-3
			14.35	0.0817	94	3-octanone	C8H16O	106-68-3
DI	III DI 1 CW R	VOC	1.99	0.11611	90	acetaldehyde	C2H4O	75-07-0
			2.83	0.09857	74	ethanol	C2H6O	64-17-5
			3.32	0.09575	94	dimethyl sulfide	C2H6S	75-18-3
			15.4	0.46557	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
DI	II DI 2 CW R	VOC	1.99	0.15138	90	acetaldehyde	C2H4O	75-07-0
			2.83	0.05484	74	ethanol	C2H6O	64-17-5
			3.32	0.06733	91	dimethyl sulfide	C2H6S	75-18-3
			15.41	1.83504	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
DI	I DI 3 CW R	VOC	1.97	0.11698	90	acetaldehyde	C2H4O	75-07-0
			2.81	0.3998	90	ethanol	C2H6O	64-17-5
			3.3	0.09924	94	dimethyl sulfide	C2H6S	75-18-3
			15.4	1.71962	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
DI	III DI 3 CW R	VOC	2	0.35215	90	acetaldehyde	C2H4O	75-07-0
			2.85	1.18755	86	ethanol	C2H6O	64-17-5
			3.33	0.08398	94	dimethyl sulfide	C2H6S	75-18-3
			5.6	0.02469	90	ethyl acetate	C4H8O2	141-78-6
			15.41	3.87204	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
Low	III 50 3 BC R	VOC	1.99	0.07182	74	acetaldehyde	C2H4O	75-07-0
			2.83	0.21222	74	ethanol	C2H6O	64-17-5
			3.31	0.08284	94	dimethyl sulfide	C2H6S	75-18-3
Low	III 50 1 BC R	VOC	1.97	0.03456	74	acetaldehyde	C2H4O	75-07-0
			3.29	0.05752	94	dimethyl sulfide	C2H6S	75-18-3
			10.73	0.09371	90	hexanal	C6H12O	66-25-1
Low	II 50 3 BC R	VOC	1.98	0.03411	74	acetaldehyde	C2H4O	75-07-0
			2.82	0.0285	74	ethanol	C2H6O	64-17-5
			3.31	0.07989	94	dimethyl sulfide	C2H6S	75-18-3
Low	I 50 2 BC R	VOC	2.02	0.03977	74	acetaldehyde	C2H4O	75-07-0
			2.84	0.07993	74	ethanol	C2H6O	64-17-5
			3.34	0.09387	91	dimethyl sulfide	C2H6S	75-18-3
Low	III 50 1 BW R	VOC	2.85	0.43382	90	ethanol	C2H6O	64-17-5
			3.33	0.11374	91	dimethyl sulfide	C2H6S	75-18-3
			9.59	0.02511	95	1-octene	C8H16O	111-66-0
			14.31	0.21024	86	1- octen-3-ol	C8H16O	3391-86-4

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			15.41	0.04839	97	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
Low	I 50 1 BW R	VOC	1.99	0.04858	74	acetaldehyde	C2H4O	75-07-0
			2.83	0.07078	74	ethanol	C2H6O	64-17-5
			3.32	0.08313	91	dimethyl sulfide	C2H6S	75-18-3
Low	III 50 3 BW R	VOC	1.97	0.07991	83	acetaldehyde	C2H4O	75-07-0
			2.65	0.03073	72	pentane	C5H12	109-66-0
			2.81	0.09665	90	ethanol	C2H6O	64-17-5
			3.3	0.16053	94	dimethyl sulfide	C2H6S	75-18-3
Low	II 50 1 BW R	VOC	1.98	0.12937	90	acetaldehyde	C2H4O	75-07-0
			2.82	0.50496	90	ethanol	C2H6O	64-17-5
			3.3	0.24365	94	dimethyl sulfide	C2H6S	75-18-3
Low	I 50 1 CW R	VOC	2	0.15546	90	acetaldehyde	C2H4O	75-07-0
			2.84	0.27214	90	ethanol	C2H6O	64-17-5
			3.28	0.07089	78	acetone	C3H6O	67-64-1
			9.59	0.03638	95	1-octene	C8H16O	111-66-0
			14.31	0.34099	78	1- octen-3-ol	C8H16O	3391-86-4
			15.4	0.60958	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
Low	III 50 3 CW R	VOC	2	0.0578	83	acetaldehyde	C2H4O	75-07-0
			2.85	0.03002	74	ethanol	C2H6O	64-17-5
			3.33	0.0604	91	dimethyl sulfide	C2H6S	75-18-3
			15.4	1.9932	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
Low	II 50 1 CW R	VOC	1.97	0.19806	90	acetaldehyde	C2H4O	75-07-0
			2.82	2.06359	90	ethanol	C2H6O	64-17-5
			3.29	0.13348	91	dimethyl sulfide	C2H6S	75-18-3
			5.58	0.07226	90	ethyl acetate	C4H8O2	141-78-6
			15.4	1.2509	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
Low	II 50 3 CW R	VOC	2.01	0.16738	90	acetaldehyde	C2H4O	75-07-0
			2.85	0.4631	90	ethanol	C2H6O	64-17-5
			3.33	0.08479	91	dimethyl sulfide	C2H6S	75-18-3
High	III 100 1 BC R	VOC	1.99	.06897NJ	90	acetaldehyde	C2H4O	75-07-0
			10.74	.04985NJ	90	hexanal	C6H12O	66-25-1
			13.16	.08037NJ	93	.alpha.-pinene	C10H16	80-56-8
			15.41	.20130NJ	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
			16.66	.02699NJ	74	1,4-pentadiene, 2,3,3-trimethyl-	C8H14	756-02-5
			15.4	0.94848	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
High	II 100 2 BC R	VOC	2.01	0.06588	74	acetaldehyde	C2H4O	75-07-0
			10.74	0.04849	90	hexanal	C6H12O	66-25-1
			15.41	0.04119	97	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
High	I 100 2 BC R	VOC	3.34	0.08673	94	dimethyl sulfide	C2H6S	75-18-3
High	III 100 2 BC R	VOC	2.01	0.10777	90	acetaldehyde	C2H4O	75-07-0
			2.84	0.13311	90	ethanol	C2H6O	64-17-5

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
			3.34	0.18058	94	dimethyl sulfide	C2H6S	75-18-3
High	BD ROOT	VOC	2	0.14556	90	acetaldehyde	C2H4O	75-07-0
			2.85	0.22719	90	ethanol	C2H6O	64-17-5
			3.34	0.29636	94	dimethyl sulfide	C2H6S	75-18-3
High	I 100 3 BW R	VOC	2.01	0.19634	90	acetaldehyde	C2H4O	75-07-0
			2.85	0.94663	90	ethanol	C2H6O	64-17-5
			3.34	0.19202	91	dimethyl sulfide	C2H6S	75-18-3
			14.35	0.08644	83	3-octanone	C8H16O	106-68-3
High	III 100 1 BW R	VOC	2	0.25164	90	acetaldehyde	C2H4O	75-07-0
			2.84	0.13391	90	ethanol	C2H6O	64-17-5
			3.33	0.29279	94	dimethyl sulfide	C2H6S	75-18-3
High	I 100 2 BW R	VOC	1.97	0.17901	90	acetaldehyde	C2H4O	75-07-0
			2.81	0.19388	90	ethanol	C2H6O	64-17-5
			3.3	0.21481	94	dimethyl sulfide	C2H6S	75-18-3
			13.16	0.02765	90	.alpha.-pinene	C10H16	80-56-8
			14.36	0.02679	91	3-octanone	C8H16O	106-68-3
High	I 100 1 BW R	VOC	2	0.07295	90	acetaldehyde	C2H4O	75-07-0
			10.74	0.05852	90	hexanal	C6H12O	66-25-1
High	I 100 2 CW R	VOC	2.01	0.46879	90	acetaldehyde	C2H4O	75-07-0
			2.85	0.37373	90	ethanol	C2H6O	64-17-5
			3.34	0.14639	94	dimethyl sulfide	C2H6S	75-18-3
			15.42	7.6618	97	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8

Table Continued

Water Trt	Sample ID	VOC or SVOC	Peak RT (min)	Estimated Concentration (mg/kg)	Quality Factor	Chemical name	Chemical formula	Cas No.
High	I 100 3 CW R	VOC	2	0.22816	90	acetaldehyde	C2H4O	75-07-0
			3.33	0.29351	94	dimethyl sulfide	C2H6S	75-18-3
			15.41	4.96324	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
High	III 100 2 CW R	VOC	2	0.33542	90	acetaldehyde	C2H4O	75-07-0
			2.86	2.42105	86	ethanol	C2H6O	64-17-5
			3.33	0.04019	80	dimethyl sulfide	C2H6S	75-18-3
			5.6	0.02817	90	ethyl acetate	C4H8O2	141-78-6
			15.42	8.37046	97	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8
High	II 100 2 CW R	VOC	1.98	0.75714	90	acetaldehyde	C2H4O	75-07-0
			2.82	0.64415	86	ethanol	C2H6O	64-17-5
			3.3	0.1664	94	dimethyl sulfide	C2H6S	75-18-3
			15.41	7.37993	98	benzaldehyde, 2- hydroxy -	C7H6O2	90-02-8

Table AD.1 June 2006 and March 2007 Caliper, Height, and Visual Data of Trees by Water Treatment

Species	Water Treatment	Mean Caliper (mm)		Mean Height (cm)		Mean Visual (1-6)	
		June	March	June	March	June	March
Bald cypress	100% NS6	11.36	19.60	95.5	126.8	4.5	4.2
	50% NS6	12.92	20.10	100.5	135.1	4.6	6.0
	100% NS2 + NS8	10.72	19.34	94.7	128.1	4.5	6.0
	67% NS2 + NS8	13.28	22.76	99.4	131.0	4.6	6.0
	33% NS2 + NS8	12.20	19.98	107.1	129.8	4.7	6.0
	33% NS2 + NS8	11.70	17.76	94.6	112.8	4.5	4.0
	DI	14.96	24.14	98.2	122.4	4.4	5.2
	DI	11.54	20.74	87.1	120.9	4.9	6.0
Black willow	100% NS6	8.46	9.90	82.4	85.4	5.0	2.8
	50% NS6	10.14	10.50	63.1	89.0	5.0	2.2
	100% NS2 + NS8	10.44	11.96	81.7	111.2	4.9	2.2
	67% NS2 + NS8	9.22	12.06	75.1	97.0	4.8	2.0
	33% NS2 + NS8	9.28	11.96	63.8	72.0	4.9	1.4
	33% NS2 + NS8	9.92	11.70	91.4	98.6	5.0	1.8
	DI	9.14	13.20	81.9	104.0	5.0	1.6
	DI	9.40	13.44	85.9	99.4	5.0	1.2
Eastern red cedar	100% NS6	10.16	13.46	65.4	94.7	5.6	2.5
	50% NS6	11.78	15.90	65.9	87.4	5.5	4.7
	100% NS2 + NS8	9.54	13.86	65.9	79.8	5.5	3.9
	67% NS2 + NS8	11.20	14.58	64.9	93.0	5.6	5.0
	33% NS2 + NS8	11.02	14.32	59.4	88.1	5.7	5.4
	33% NS2 + NS8	12.92	17.14	63.1	81.0	5.7	5.2
	DI	11.68	13.76	65.5	81.3	5.5	5.3
	DI	11.82	15.62	63.9	91.9	5.4	4.9
Spruce pine	100% NS6	3.90	5.80	28.6	40.6	5.6	3.3
	50% NS6	4.06	5.40	29.5	39.0	5.8	2.8
	100% NS2 + NS8	4.30	5.62	37.3	36.2	5.3	1.2

Table Continued

Species	Water Treatment	Mean Caliper (mm)		Mean Height (cm)		Mean Visual (1-6)	
		June	March	June	March	June	March
Spruce pine	67% NS2 + NS8	5.66	7.32	38.4	51.6	5.7	4.4
	33% NS2 + NS8	5.04	5.66	34.7	45.6	5.6	3.3
	33% NS2 + NS8	4.08	6.85	32.5	47.5	5.3	3.1
	DI	4.68	6.80	30.5	50.2	5.7	3.6
	DI	5.64	6.98	38.0	49.2	5.7	4.4
Water oak	100% NS6	5.64	10.16	47.1	63.0	5.1	3.0
	50% NS6	6.50	11.42	51.6	89.0	5.4	2.6
	100% NS2 + NS8	6.40	12.48	64.6	79.0	5.3	2.2
	67% NS2 + NS8	7.28	11.78	52.8	85.2	5.1	3.0
	33% NS2 + NS8	5.74	11.70	46.7	94.4	5.3	2.8
	33% NS2 + NS8	4.88	11.86	54.5	83.6	5.4	3.0
	DI	7.24	12.38	49.0	94.4	5.2	2.2
	DI	7.14	12.48	57.4	110.0	5.2	3.6

Visual scale 1-6; 1 = dead or no green leaves; 3 = 50% green leaves 50% brown or yellow; 6 = all green leaves.

VITA

Kathryn Fontenot was born in Fort Worth, Texas, to Kenneth and Marlys Karsh. After completing high school, she began studies at Louisiana State University. She received her Bachelor of Science degree in psychology in May of 2003 and her Master of Science degree in horticulture in May of 2005. At the 2009 spring commencement she will be awarded the doctoral degree in the field of horticulture.